The esters, amides and anilides of the acids were prepared from the acid chlorides in benzene solution by treatment with the corresponding reagent.

**Basic Esters and Amides of Diphenoxyacetic Acid.**—Eight parts of diphenoxyacetic acid[12] was refluxed in benzene solution with seven parts of purified thionyl chloride for six to seven hours, and the mixture was allowed to stand overnight. Benzene and thionyl chloride were stripped under reduced pressure, and the crude acid chloride[9] was used in the next step.

Equivalent amounts of diphenoxyacetyl chloride and the dialkylaminoalkanol, or dialkylaminoalkylamine, respectively, were mixed in benzene solution. After an initial exothermic reaction the hydrochlorides of the reaction products precipitated, and usually solidified after some standing. In selected cases, the bases were liberated with sodium bicarbonate solution, and purified if they were more readily handled than the salts.

**Isoamyl *o*-Phenylenedioxyacetate.**—The preparation of this ester was patterned on that reported for the ethyl ester.[13] The preparative modification described here produced the isoamyl ester in a yield of 16.7% as compared with 8% reported for the ethyl ester.[14]

To a hot solution of 106 g. of sodium in 1200 cc. of dry isoamyl alcohol was added a suspension of 254 g. of catechol in 250 cc. of isoamyl alcohol with stirring in an atmosphere of nitrogen. The resulting viscous white mass was heated at 120° and treated gradually with 362 g. of ethyl dichloroacetate at such a rate that the exothermic reaction subsided after about one-half of the ester had been added. The reaction mixture became fluid and turned purple. It was refluxed another sixteen hours, 700 cc. of isoamyl alcohol was distilled off at 20 mm. pressure, and the dark viscous residue was dissolved in 2 liters of ether. The ether solution was washed with several liters of an ice-cold calcium chloride solution, and then with two 500-cc. portions of cold 2% sodium hydroxide solution. The dark red ether layer was dried over calcium chloride, the solvent was distilled, and the residual oil was fractionated several times. The colorless fraction boiling finally at 149–152° (20 mm.) weighed 90 g. (16.7%). It consisted of practically pure isoamyl *o*-phenylenedioxyacetate but gave a weak test for catechol. Repeated fractionation to b. p. 122–124° (2 mm.) furnished a satisfactory analytical sample.

(12) Auwers and Haymann, *Ber.*, **27**, 2795 (1894).

(13) Christiansen and Dolliver, THIS JOURNAL, **66**, 312 (1944).

(14) Dolliver, private communication.

*Anal.* Calcd. for $C_{13}H_{16}O_4$: C, 66.10; H, 6.78. Found: C, 66.05; H, 7.00.

***o*-Phenylenedioxyacetic Acid.**—A mixture of 13 g. of isoamyl *o*-phenylenedioxyacetate and 75 cc. of 8% sodium hydroxide solution was heated at 90° for forty-five minutes; isoamyl alcohol was extracted with ether, and the colorless solution was acidified and extracted with ether. After drying over sodium sulfate, the solvent was removed, and the residual oil was allowed to crystallize from petroleum ether. The yield of colorless flakes, m. p. 104–106°, was 6 g. (65.6%). The material gave no ferric chloride test for catechol, and did not depress the melting point of an authentic sample[13].

***o*-Phenylenedioxyacetamide.**—When dry ammonia was passed through isoamyl *o*-phenylenedioxyacetate at 100°, the ester became cloudy, and the product cleared and solidified after thirty minutes. The colorless amide crystallized from ether–petroleum ether, m. p. 105–106°. It gave no color test with ferric chloride, and could be hydrolyzed with 25% sodium hydroxide solution at room temperature.

*Anal.* Calcd. for $C_8H_7NO_3$: N, 8.41. Found: N, 8.62.

The amide could also be prepared in poor yields, from *o*-phenylenedioxyacetyl chloride which was obtained from the acid and thionyl chloride in benzene solution. This acid chloride could not be purified but served also as the starting material for the preparation of the unstable diethylaminoethyl *o*-phenylenedioxyacetate.

## Summary

The condensation of several aromatically and heterocyclically substituted ethylene derivatives with ethyl diazoacetate furnished the ethyl esters of the corresponding cyclopropanecarboxylic acids. Dialkylaminoalkyl esters of some of these acids were prepared as potential antispasmodics.

A series of dialkylaminoalkyl diphenoxyacetates and diphenoxyacetamides was prepared for comparison with the isosteric derivatives of dibenzylacetic acid. The chemical stability of the acetal type derivatives of diphenoxyacetic acid was compared with that of similar compounds derived from *o*-phenylenedioxyacetic acid.

CHARLOTTESVILLE, VIRGINIA RECEIVED MARCH 23, 1949

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

# The Synthesis of Some 1-Cyclopentenealdehydes

BY JAMES ENGLISH, JR., AND GEORGE W. BARBER[1]

In many of the possible synthetic approaches[2] to molecules having structures analogous to auxin a[3] substituted 1-cyclopentenealdehydes are necessary starting materials. The preparation of such substances has therefore been undertaken with a view to their eventual utilization in a synthetic program.

1-Cyclopentenealdehyde itself has been prepared by the rearrangement of cyclohexene peroxide[4] and from adipic aldehyde obtained by ozonolysis of cyclohexene.[5] Urion obtained this substance also by treatment of divinylglycol with alumina at 300°.[6] These methods, however, are not easily adapted to the preparation of substituted 1-cyclopentenealdehydes and in our experience have given unsatisfactory yields. The process finally developed is shown in the equations.

The 3-*n*-propyl- and 3,5-di-*n*-propylpyrocatechols were prepared from the corresponding allyl derivatives by hydrogenation; the allyl pyrocate-

(1) Present address: Cox Medical Research Institute, University of Pennsylvania. Taken from a thesis submitted by George W. Barber to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the Ph.D. degree.

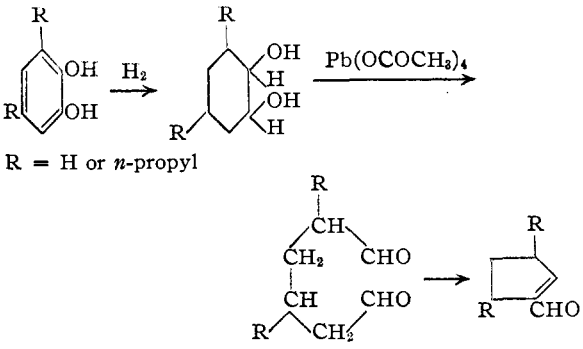
(2) J. English and J. D. Gregory, THIS JOURNAL, **69**, 2123 (1949).

(3) F. Kogl, *Ber.*, **68A**, 16 (1935).

(4) E. W. Farmer and A. Sundralingham, *J. Chem. Soc.*, 121 (1942).

(5) A. Wohl and H. Schweiger, *Ber.*, **39**, 895 (1906).

(6) E. Urion, *Ann. chim.*, [11] **1**, 5 (1934).




chols in turn were obtained from guaiacol and eugenol, respectively, as described in the literature. Pyrocatechol and its mono- and di-propyl derivatives were hydrogenated with Raney nickel to give the corresponding cyclohexanediols in 84–86% yields. No attempt was made to separate the *cis* and *trans* forms of these compounds, but the redistilled mixtures were oxidized with lead tetraacetate in benzene or chloroform. It was found that by the addition of anhydrous potassium carbonate to the reaction mixture to maintain neutrality, the losses in handling the resulting adipic aldehydes were much decreased in comparison with those experienced in the original procedure of Criegee.[7]

After considerable experimentation the method of Wohl and Schweitzer[5] was found most effective for the cyclization of adipic aldehydes and yields of about 50% of the corresponding 1-cyclopentenealdehyde were obtained directly from the lead tetraacetate oxidation mixture without the necessity of isolating the intermediate adipic aldehydes. In the case of 3,5-di-*n*-propyladipic aldehyde cyclization took place during the oxidation reaction, especially in chloroform solution, and a yield of 80% of 3,5-di-*n*-propyl-1-cyclopentenealdehyde was obtained directly.

The structures proposed for the cyclization products of the 3-*n*-propyl- and 3,5-di-*n*-propyladipic aldehydes are supported by the loss of water of the intermediate aldols during the cyclization. By analogy with other aldol condensations as reported in the literature,[8] no such dehydrations would have been expected if the cyclization had involved the tertiary alpha carbon atom. In analogous base-catalyzed cyclizations of the Dieckmann type a similar phenomenon is observed.[9] Here again a secondary alpha carbon atom rather than a tertiary one seems always to be involved.

Attempts were made to separate the 3,5-di-*n*-propyl-1-cyclopentenealdehyde into its *cis* and *trans* forms. The hydrogenation of pyrocatechol has been found[10] to give a mixture of isomers and similar behavior might have been expected in this case. However, neither extensive fractional crystallization of the semicarbazone or a careful fractional distillation produced any evidence of the existence of significant amounts of an isomer in the purified material. It therefore seems probable that this substance is homogeneous, and that the hydrogenation of disubstituted catechols leads to a predominance of one stereoisomer, probably *trans* with respect to the alkyl groups.

On standing at room temperature all three 1-cyclopentenealdehydes were observed to polymerize, becoming yellow and viscous in the course of a few days. Preliminary experiments indicate that the freshly prepared propyl-1-cyclopentenealdehydes react normally in the Reformatski reaction with ethyl bromoacetate.

## Experimental[11]

**3-*n*-Propylpyrocatechol.**—A mixture of 442 g. of 6-propylguaiacol, b. p. 80–82° at 1.5 mm., prepared from 6-allylguaiacol[12] by hydrogenation with platinum oxide at 50 p. s. i. in ethanol, was refluxed for twelve hours in a solution of 750 g. 48% hydrobromic acid in 1 liter of glacial acetic acid. After removal of the excess hydrobromic acid and solvent the residue was distilled. There was obtained 382 g. (95% of theory) of colorless 3-propylpyrocatechol, b. p. 112–113° at 1.5 mm. On recrystallization from ethanol the product melted at 72°. Kurosawa[13] reported the melting point of this substance as 70–72°.

**3,5-Di-*n*-propylpyrocatechol.**—Diallylguaiacol, prepared by the method of Claisen and Eisleb[14] was hydrogenated in ethanol with platinum oxide at 60 p. s. i. The product, obtained in quantitative yield was 4,6-di-*n*-propylguaiacol, b. p. 107–108° at 1 mm., $n^{20}D$ 1.5123. A dinitrobenzoate was prepared m. p. 117.5°. *Anal.* Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.13; H, 9.72. A mixture of 208 g. of this product was refluxed with 300 cc. of 48% hydrobromic acid and 800 cc. of glacial acetic acid for eight hours. After evaporation of the residual hydrobromic acid and solvent *in vacuo*, the product was distilled, b. p. 115–120° at 1 mm., as a viscous liquid that slowly crystallized. On recrystallization from petroleum ether (b. p. 30–60°) by cooling in Dry Ice there was obtained 169 g. (87%) of crystalline 3,5-di-*n*-propylpyrocatechol, m. p. 39–40°. The pure product melts at 41.5°.

*Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.19, H, 9.34. Found: C, 74.18; H, 9.04.

**Hydrogenation of Pyrocatechols.**—Pyrocatechol and the above substituted pyrocatechols were hydrogenated in 100 g. batches with 50 cc. of absolute ethanol, 10 g. of Raney nickel and a pellet of sodium hydroxide.[15] The reaction was carried out at about 2000 p. s. i. and at a temperature of 140 to 160°. Six to nine hours were required for complete hydrogenation, the higher homologs requiring the longer times. The products were taken up in petroleum ether, washed with 10% sodium hydroxide to remove any unchanged pyrocatechol, and the residues distilled after evaporation of the solvent. The properties and yields of the mixtures of stereoisomeric cyclohexanediols obtained were:

| | B. p. °C. | Mm. | Yield, % | M. p., °C. |
|---|---|---|---|---|
| 1,2-Cyclohexanediols[16] | 110–115 | 5 | 84 | 72–80 |

(7) R. Criegee, *Ber.*, **64**, 264 (1931).

(8) A. Lieben, *Monatsh.*, **22**, 289 (1901).

(9) W. Dieckmann, *Ann.*, **317**, 27 (1901); A. Kötz and P. Schuller, *Ann.*, **350**, 234 (1906); R. Cornubert and C. Bonel, *Bull. soc. chim.*, [4] **47**, 300 (1930).

(10) L. W. Covert, R. Connor and H. Adkins, THIS JOURNAL, **54**, 1658 (1932).

(11) All melting and boiling points are corrected.

(12) L. Claisen, *Ber.*, **45**, 3161 (1912).

(13) J. Kurosawa, *ibid.*, **48**, 1603 (1915).

(14) L. Claisen and O. Eisleb, *Ann.*, **401**, 21 (1913).

(15) H. E. Ungnade and D. V. Nightingale, THIS JOURNAL, **66**, 1218 (1944).

(16) Amatatsu, *J. Chem. Soc. Japan*, **52**, 585 (1931); *Chem. Abstr.*, **26**, 5084 (1931).

| | B. p. °C. | Mm. | Yield, % | M. p. °C. |
|---|---|---|---|---|
| 3-*n*-Propyl-1,2-cyclohexanediols | 121–122 | 4 | 87 | |
| 3,5-Di-*n*-propyl-1,2-cyclohexanediols | 135–150 | 2 | 86 | |

**Adipic Aldehyde.**[7]—Twenty grams (0.17 mole) of the above 1,2-cyclohexanediol preparation was dissolved in 200 cc. of dry benzene and 50 g. anhydrous potassium carbonate added. The mixture was stirred vigorously while 76 g. (0.17 mole) of lead tetraacetate was added in 5 g. portions over the course of one hour. A nitrogen atmosphere was maintained during the addition and subsequent distillations. The mixture was stirred for an additional hour after the addition was complete and then filtered. The mixture of salts was extracted thoroughly with benzene and the combined filtrates dried briefly over sodium sulfate. The benzene was then removed in vacuum and the product distilled. There was obtained 13.4 g. (68%) of colorless adipic aldehyde, b. p. 68–70 at 3 mm., $n^{20}D$ 1.4350. There was always observed a higher boiling fraction of polymerized material and a non-volatile residue.

**1-Cyclopentenealdehyde.**[5]—Nineteen grams of freshly distilled adipic aldehyde was heated with 115 cc. of distilled water in a bomb at 110° for five hours. After cooling, the solution was then extracted thoroughly with ether and the product isolated by distillation. There was obtained 10 g. of 1-cyclopentenealdehyde (62%), b. p. 57–59° at 23 mm., $n^{20}D$ 1.4866.

An over-all yield of 52% was obtained by treating the crude adipic aldehyde as obtained above on evaporation of solvent with water at 110° in the same manner. The product in both cases polymerized on standing. Urion reported the properties of this substance as: b. p. 48° at 11 mm., $n^{20}D$ 1.4828.

**2-*n*-Propyladipic Aldehyde.**—The 3-*n*-propylcyclohexane-1,2-diol mixture described above (30 g.) was oxidized in the same manner as described above for cyclohexanediol. There was obtained 19.5 g. (68%) of 2-*n*-propyladipic aldehyde, b. p. 124–127° at 15 mm. Careful fractionation gave a product b. p. 83° at 2 mm., $n^{20}D$ 1.4478, $d_{20}$ 0.9580; molecular refraction calcd., 43.8; found, 43.6.

The 2,4-dinitrophenylhydrazone prepared in the usual manner melted at 178–179° after recrystallization from glacial acetic acid.

*Anal.* Calcd. for $C_{21}H_{24}N_8O_8$: C, 48.84; H, 4.68. Found: C, 49.42; H, 4.63.

**2-*n*-Propyladipic acid**[17] was prepared by heating 5.2 g. of 2-*n*-propyladipic aldehyde in 100 cc. of water and 50 cc. of alcohol with 20 g. of fresh silver oxide and 3 g. of sodium hydroxide. After two hours of refluxing and stirring the mixture was filtered and extracted with ether. After acidification with hydrochloric acid, the solution was again extracted with ether yielding, on removal of the solvent, an oil that crystallized partially after standing some time. On recrystallization from petroleum ether (b. p. 30–60°) 2-*n*-propyladipic acid m. p. 53–54° was obtained.

*Anal.* Calcd. for: $C_9H_{16}O_4$: C, 57.43; H, 8.57; neut. equiv., 94.1. Found: C, 57.38; H, 8.55; neut. equiv., 95.1.

**3-*n*-Propyl-1-cyclopentenealdehyde.**—A 63% yield of this substance was obtained from 15 g. of 2-propyladipic aldehyde by the procedure described above for 1-cyclopentenealdehyde. By treating the undistilled 2-propyladipic aldehyde directly with water at 110° as described above, an over-all yield of 52% of 3-propyl-1-cyclopentenealdehyde b. p. 86–88° at 15 mm. was obtained. The semicarbazone prepared in the usual manner and recrystallized from dilute ethanol melted at 188–189°.

*Anal.* Calcd. for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.58; H, 8.86; N, 20.91.

Steam distillation of a mixture of 7.8 g. of this semicarbazone with 7 g. of oxalic acid in 200 cc. of water yielded pure 3-*n*-propyl-1-cyclopentenealdehyde (3.5 g.), b. p. 54–55° at 2 mm., $n^{20}D$ 1.4780; $d_{20}$ 0.9285; molecular refraction calcd. 41.11, found 42.13 (exaltation 2.5%). The 2,4-dinitrophenylhydrazone was obtained by crystallization from dilute alcohol as bright red needles, m. p. 149°.

**3,5-Di-*n*-propylcyclopentenealdehyde.**—Oxidation of 50 g. of the 3,5-di-*n*-propylcyclohexane-1,2-diol mixture in 300 cc. of dry chloroform containing 40 g. of anhydrous potassium carbonate in the same manner as described for the oxidation of cyclohexanediol, yielded on distillation 35.9 g. (80%) of 3,5-di-*n*-propyl-1-cyclopentenealdehyde b. p. 106–107° at 3.5 mm., $n^{20}D$ 1.4730. Under these conditions there seemed to be little if any of the di-*n*-propyl adipic dialdehyde formed. When benzene was substituted for chloroform, the details being otherwise the same, there was obtained 24.8 g. of material boiling at 95–120° at 2 mm.; refractionation yielded in addition to 3,5-di-*n*-propylcyclopentenylformaldehyde about 3 g. of a higher fraction, b. p. 112° at 2 mm., $n^{20}D$ 1.4554, which was presumably the di-*n*-propyladipic dialdehyde. This fraction was not further investigated. The semicarbazone, prepared in dilute alcohol and recrystallized from alcohol, melted at 124.5–125°.

*Anal.* Calcd. for $C_{13}H_{23}N_3O$: C, 65.79; H, 9.77; N, 17.71. Found: C, 65.72; H, 9.55; N, 17.57.

An attempt at separation of the possible stereoisomers by fractional crystallization of the semicarbazones yielded only the product described above and a small amount of non-crystalline oil. This oil may have contained other isomeric forms, but has not been investigated further. Careful fractional distillation of 35 g. of freshly prepared 3,5-di-*n*-propylcyclopentenylformaldehyde yielded an apparently homogeneous product, b. p. 89–90° at 3.5 mm., *n* 1.4735 to 1.4740; a total of 19 fractions were collected arbitrarily from a 40 cm. column packed with steel helices (about 25 theoretical plates) and 24.5 g. of material fell within the range given above. The remainder was largely polymerized residue in the still pot. Semicarbazones from these fractions melted at 124–125° as before. On standing at room temperature the free aldehyde became viscous due to polymerization.

**Ethyl 3-(3-*n*-Propyl-1-cyclopentenyl)-3-hydroxypropionate.**—A solution of 9 g. of 3-*n*-propyl-1-cyclopentenealdehyde and 16.7 g. of ethyl bromoacetate in a mixture of 16 cc. of dry benzene and 4 cc. of ether was added slowly under nitrogen to 7 g. of activated[18] zinc dust. The rate of addition was adjusted to maintain gentle reflux. After the addition the mixture was heated for one hour, the excess zinc removed and 100 cc. of ether added. The mixture was shaken alternately with dilute sulfuric acid and sodium bicarbonate until no cloudiness appeared on bicarbonate treatment and the product finally distilled under reduced pressure. After careful fractionation 6.6 g. (45%) of pure ethyl 3-(3-*n*-propyl-1-cyclopentenyl)-3-hydroxypropionate, b. p. 128 at 2 mm., $n^{20}D$ 1.4688, $d_{20}$ 0.9975 was obtained.

*Anal.* Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.46; H, 9.93.

**Ethyl 2-(3,5-Di-*n*-propyl-1-cyclopentenyl)-3-hydroxypropionate.**—This ester was prepared in the same way from 3,5-di-*n*-propylcyclopentenealdehyde and ethyl bromoacetate. The ester, obtained in 50% yield, was carefully fractionated in vacuum. Pure ethyl (3,5-di-*n*-propyl-1-cyclopentenyl)-3-hydroxypropionate boiled at 124° at 1 mm., $n^{20}D$ 1.4686, $d_{20}$ 0.9688.

*Anal.* Calcd. for $C_{16}H_{28}O_3$; C, 71.60; H, 10.52. Found: C, 70.69; H, 10.17.

The free acids corresponding to both of the above hydroxy esters were prepared by hydrolysis in alcoholic potassium hydroxide at room temperature. Both were obtained as liquids which defied attempts at crystallization. The product obtained from the monopropyl analog gave

(17) J. W. Mellor, *J. Chem. Soc.*, **79**, 131 (1901).

(18) R. L. Shriner, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. I, p. 16.

evidence of containing some lactone. The nature of these compounds will be further investigated.

## Summary

A practical synthesis of substituted 1-cyclopentenealdehydes has been developed and applied to 1-cyclopentenealdehyde, 3-*n*-propyl-1-cyclopentenealdehyde and 3,5-di-*n*-propyl-1-cyclopentenealdehyde.

The substituted 1-cyclopentenealdehydes have been shown to undergo the Reformatski reaction.

NEW HAVEN, CONNECTICUT RECEIVED MARCH 17, 1949

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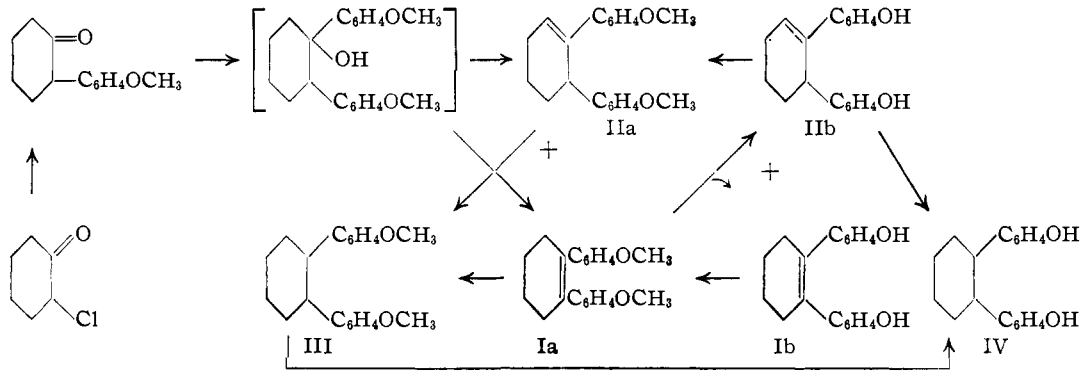
[CONTRIBUTION NO. 67 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

# Synthesis of Cyclohexestrol[1]

BY GEORGE P. MUELLER AND ROY MAY[2]

Much of the search for new synthetic estrogens has consisted either of substituting groups within the essentially intact hexestrol skeleton, or of building other structures also supposedly capable of simulating the nuclear form of the estrogenic hormone. The synthesis of the cyclohexane analog, for which previous attempts have been reported,[3] has been completed.




The formation of 2-substituted cyclohexanones from 2-chlorocyclohexanones has been studied more recently by Mousseron[4] and by Newman[5] who have shown that the alkyl or aryl group from an attacking Grignard reagent may become attached either to the carbonyl or the halogen-bearing carbon. Our results indicate further either that a 2-substituted cyclohexanone or cyclohexene oxide is formed and subject to further attack as in the formation of tertiary alcohols from carboxylic esters, or that the halogen-bearing and carbonyl carbons are attacked simultaneously. Thus, although clean separations of products were difficult, a 2:1 mole ratio of *p*-methoxyphenylmagnesium bromide to 2-chlorocyclohexanone favored the formation of bis-(*p*-methoxyphenyl)-cyclohexenes, Ia and IIa, over that of 2-*p*-methoxyphenylcyclohexanone,[6] and conversely for a 1:1 ratio.

The mixture of cyclohexenes must have been formed by spontaneous dehydration during the reaction or on hydrolysis of the magnesium salts, since the isomer Ia was on one occasion crystallized directly from the crude products before application of the usual dehydrating conditions.

Parmerter[7] obtained a 1,2-diphenylcyclohexene after dehydrating the crude hydrolysis product from phenylmagnesium bromide and 2-phenylcyclohexanone, but he did not confirm the actual presence of a carbinol. Further evidence of the activating effect of the *p*-methoxyphenyl group in this connection was observed during a synthesis of 2-*p*-methoxyphenylcyclohexanone through perbenzoic acid oxidation of 1-*p*-methoxyphenylcyclohexene. Here, distillation of the acid-free oxidation product to purify the 1-*p*-methoxyphenylcyclohexene oxide yielded instead the cyclohexanone. 1-Phenylcyclohexene oxide was reported however as being purified in this way and requiring acid catalysis to effect the rearrangement.[8]

Two bis-(*p*-methoxyphenyl)-cyclohexenes, Ia and IIa, were isolated and separately hydrogenated to the same cyclohexane, III, which was demethylated in alcoholic alkali to 1,2-bis-(*p*-hydroxyphenyl)-cyclohexane IV. We have called

(1) The main portion of this paper was presented at the American Chemical Society meeting at Washington, D. C., September, 1948.

(2) Present address: T. V. A., Health and Safety Dept., Wilson Dam, Alabama.

(3) (a) Price and Mueller, THIS JOURNAL, **66**, 628 (1944); (b) **66**, 632 (1944).

(4) Mousseron, Granger, Winternitz and Combes, *Bull. soc. chim.*, 610 (1946).

(5) Newman and Booth, *J. Org. Chem.*, **12**, 737 (1947).

(6) Shortly after its preparation in this laboratory this ketone was reported by Bachmann and Wick at the American Chemical Society Meeting, Chicago, Ill., 1948.

(7) Parmerter, THIS JOURNAL, **71**, 1127 (1949).

(8) Sherwood, Short and Woodcock, *J. Chem. Soc.*, 323 (1936).