3,5-dinitrobenzoate in a 250-ml. Erlenmeyer flask was added rapidly with vigorous shaking during 15 seconds 75 ml. of 0.5 *N* sodium hydroxide in alcoholic solution. The flask was immersed immediately in a salt–ice cooling mixture. The resulting red solution was acidified as fast as possible (about 30 sec.) with concentrated sulfuric acid, with careful avoidance of any pronounced rise in temperature. The solution became first blue, and colorless when acidic. It was made alkaline again with solid sodium carbonate, regenerating the blue color, and strong cooling was continued in order to separate from the solution most of the salts. The precipitate (P) was filtered and thoroughly washed with cooled anhydrous ethanol. The washings were added to filtrate and concentrated. The resulting mixture of ester and salts was treated with a small amount of water and filtered, giving solid (P'). The filtrate was extracted twice with ether. (If the ethereal solution turns color it is desirable to wash it with a little water.) The ethereal solution (S) contained the ethyl 2-hydroxycyclopentanecarboxylate. The solid (P) was extracted with water, yielding solid (P''). The aqueous extract was extracted twice with ether, and the resulting ethereal solution (S') was added to (S), and the solvent evaporated. The residue was distilled at 0.1–0.2 mm., and most of the material boiled at about 55°. The distillate did not decolorize a dilute potassium permanganate solution. The esters are fairly hygroscopic. (P') and (P'') were unchanged 3,5-dinitrobenzoates. The aqueous solution gave 3,5-dinitrobenzoic acid on acidification. From 10 g. of 3,5-dinitrobenzoate, m.p. 116.0–116.8°, we obtained 2.9 g. of ethyl *cis*-2-hydroxyclopentanecarboxylate the constants of which are reported in Table II, and 0.5 g. of non-hydrolyzed product.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.91. Found: C, 61.08, 60.86; H, 8.97, 9.05.

From 7.4 g. of 3,5-dinitrobenzoate, m.p. 76.2–77.1°, we obtained 2.6 g. of ethyl *trans*-2-hydroxycyclopentanecarboxylate (see Table II for the physical constants), and 0.7–0.8 g. of unchanged dinitrobenzoate.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.91. Found: C, 60.38, 60.78; H, 9.01, 9.00.

Preparation of the *cis*- and *trans*-2-Hydroxycyclopentanecarboxylic Acids.—For the hydrolysis of the pure hydroxy esters saturated aqueous barium hydroxide solution may be used, or, more conveniently, 0.5 *N* aqueous sodium hydroxide. The amount of base used was 1.5 equivalents. A few minutes after mixing of the reactants the system became homogeneous, and was then ready to be acidified with concentrated sulfuric acid with cooling. After saturation with ammonium sulfate, the solution was extracted several times with ether. The ethereal solution was dried over sodium sulfate and evaporated. In the case of the *cis*-hydroxy acid, an oily substance resulted which crystallized on rubbing in the cold. After two recrystallizations from ether, in which it is extremely soluble, and from ligroin, the product melted at 52–53.4°. It is deliquescent and for this reason the melting points were determined in sealed capillary tubes. Distillation under atmospheric pressure gave cyclopentene-1-carboxylic acid.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.61, 55.31; H, 7.88, 7.72.

In the case of the *trans*-hydroxy acid, the oily substance resulting after the removal of the solvent crystallized easily. Recrystallization from ether and from ligroin gave transparent tablets melting at 68.3–69.0°. It is very soluble in water but not deliquescent, and is somewhat less soluble in ether than its isomer. It eliminated water on distillation at atmospheric pressure, similar to the *cis*-hydroxy acid.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.43, 55.68; H, 7.76, 7.89.

The Hydrazides of the *cis*- and *trans*-2-Hydroxycyclopentanecarboxylic Acids. *cis*-Hydrazide.—To a mixture of 1 g. of *cis*-hydroxy ester and 0.5 g. of hydrazine hydrate a little more ethanol than the amount required for complete dissolution was added. The mixture was refluxed for three hours. After removal of the solvent the residue gave, on cooling, 0.2 g. of white product, which, recrystallized from methanol, melted at 155.8–156.5°.

***trans*-Hydrazide.**—The foregoing procedure was followed, but a much more extended heating was required (16 hours). The derivative crystallized somewhat less easily on being left overnight in a desiccator. The product was dried on a porous plate. The product was recrystallized from methanol–ether. It is very soluble in water, but practically insoluble in anhydrous ether. The amount of this derivative which we obtained was too small for a good analysis. For the same reason it was not possible to get a good melting point; needles, m.p. 135.3–137.2°. A mixed melting point with the *cis*-hydrazide gave a depression.

Anal. Calcd. for $C_6H_{12}O_2N_2$: N, 19.43. Found: N, 18.72, 18.65.

BARCELONA, SPAIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Stereochemistry of the Reaction of Benzoin and Related Compounds with the Grignard Reagent[1]

BY DAVID Y. CURTIN,[2] ELBERT E. HARRIS AND ESTELLE K. MEISLICH

cis- and *trans*-1-*p*-anisyl-1,2-diphenylethylene have been prepared by a route which leads to their configurational assignment. The two olefins have been oxidized with osmium tetroxide to *dl-erythro*- and *dl-threo*-1-*p*-anisyl-1,2-diphenylethylene glycol, respectively. This determination of the configuration of the glycols has made possible the elucidation of the stereochemical course of the reaction of benzoin with anisylmagnesium bromide and the reaction of 4-methoxybenzoin with phenylmagnesium bromide. Similarly, the reaction of benzoin methyl ether with anisylmagnesium bromide and the reaction of 4-methoxybenzoin methyl ether with phenylmagnesium bromide have been shown to be stereospecific and to follow the same stereochemical course as the reactions of the benzoins. The steric course of these reactions has been compared with that of a number of Grignard reactions with desylamines.

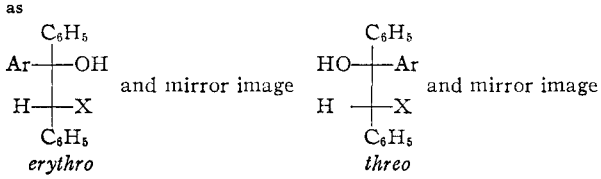
Benzoin has been shown to react with *p*-anisylmagnesium bromide to give a *dl*-1,2-diphenyl-1-*p*-anisylethylene glycol (I) which was designated "α," while 4-methoxybenzoin reacted with phenylmagnesium bromide to give the "β" racemate.[3] However, the configurations of "α"- and "β"-I were unknown. It has now been possible to establish the configurations of "α"- and "β"- I as *erythro*- and *threo*,[4] respectively, by the method described below.

(1) Abstracted in part from the Ph.D. Thesis submitted by Elbert E. Harris to Columbia University.

(2) Department of Chemistry, University of Illinois, Urbana, Illinois.

(3) A. Orekoff and M. Tiffeneau, *Bull. soc. chim.*, [4] **29**, 445 (1921); A. McKenzie, E. M. Luis, M. Tiffeneau and P. Weill, *ibid.*, [4] **45**, 414 (1929).

(4) In this work the designations "*erythro*" and "*threo*" will be used as



erythro *threo*

Koelsch[5] had previously synthesized and established the configuration of *cis*- and *trans*-α-*p*-anisyl-α,β-diphenylacrylic acid (*cis*- and *trans*-II). These acids were prepared and decarboxylated with copper chromite in boiling quinoline, a method which has been shown with similar compounds to lead to retention of configuration around the ethylenic linkage.[6] Decarboxylation of *trans*-II gave, after purification of the product by chromatography, a single olefin, *trans*-III, in 60% yield. Decarboxylation of *cis*-II, under the same conditions, gave, after purification of the product by chromatography, 30% of *cis*-III, 25% of *trans*-III and 45% of an oily mixture which did not crystallize. The use of the decarboxylation reaction to establish the configurations of *cis*- and *trans*-III is less satisfactory than it would have been had *cis*-II given a single olefin. The most probable explanation of the results would appear to be that *cis*-II did, in fact, give only *cis*-III on decarboxylation but that either *cis*-II or *cis*-III was partially isomerized to the *trans*-series during the course of the decarboxylation reaction. That these configurational assignments to the olefins are correct is supported by the results to be reported below.

Osmium tetroxide oxidation was now used to relate *dl* "α"- and "β"-I to *cis*- and *trans*-III. It was found that *cis*-III, on treatment with osmium tetroxide gave a single *dl*-glycol, *dl*-"α"-I, while *trans*-III gave only *dl*-"β"-I. Since osmium tetroxide has been shown to undergo *cis*- addition to olefins,[7] "α"-I is *erythro* and the "β"-I *threo*. The steric course of each of the Grignard reactions is shown in Fig. 1, together with the reactions used to relate *threo*-I to *trans*-II. Only one member of each racemate of I is shown.

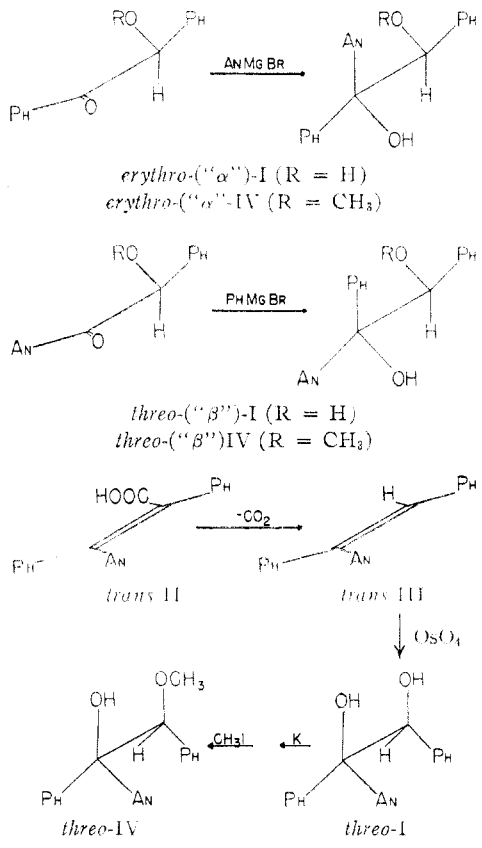
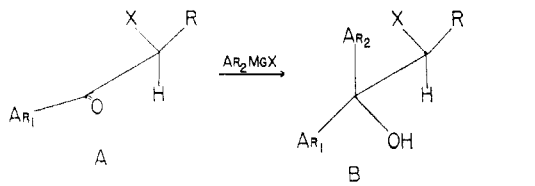


Fig. 1.

Attempts to relate the olefins, *cis*- and *trans*-III, to the corresponding oxides by reaction with perbenzoic acid failed. *cis*- or *trans*-III could be converted to an ethylene oxide by treatment with bromine in aqueous solution and ring-closure of the bromohydrin thus formed. However, each olefin gave the same oxide.

The stereochemistry of the reaction of two benzoin methyl ethers with the Grignard reagent was also examined. When *dl*-benzoin methyl ether was treated with anisylmagnesium bromide, a single racemate of 1,2-diphenyl-1-*p*-anisyl-2-methoxyethanol(IV) was obtained in 63% yield. That this racemate has the *erythro*- configuration was shown by its preparation from the reaction of the potassium salt of *dl-erythro*-I with methyl iodide. Similarly, when *dl*-4-methoxybenzoin methyl ether was treated with phenylmagnesium bromide, only *dl-threo*-IV (60% yield) was isolated. Its configuration was confirmed by its preparation from the potassium salt of *dl-threo*-I in 40% yield.

TABLE I



Ar_1 X = NH_2	Ar_2 R = C_6H_5	Yield of adduct, %
Phenyl	*p*-Anisyl	60[8b,11a]
p-Anisyl	Phenyl	50[9,11a]
Phenyl	*p*-Chlorophenyl	30[8c]
p-Chlorophenyl	Phenyl	40[8c]
Phenyl	α-Naphthyl	50[13]
Phenyl	*p*-Tolyl	60[11a,8c]
p-Tolyl	Phenyl	85[9,11a,12]
X = NH_2	R = CH_3	
Phenyl	*p*-Tolyl	60[8c,11a]
p-Tolyl	Phenyl	60[8c,11a]
X = OH	R = C_6H_5	
Phenyl	*p*-Anisyl	70[3,11b]
p-Anisyl	Phenyl	70[3,11b]
X = OCH_3	R = C_6H_5	
Phenyl	*p*-Anisyl	65[11b]
p-Anisyl	Phenyl	60[11b]

(5) C. F. Koelsch, THIS JOURNAL, **54**, 2487 (1932).

(6) See D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716 (1951), for a discussion (with earlier references) of this point.

(7) (a) R. Criegee, *Ann.*, **522**, 75 (1936); (b) R. Criegee, B. Marchand and H. Wannowius, *ibid.*, **550**, 99 (1942).

(8) (a) A. McKenzie and A. K. Mills, *Ber.*, **62**, 1784 (1929); (b) A. McKenzie, A. K. Mills and J. R. Myles, *ibid.*, **63**, 904 (1930); (c) M. Tiffeneau, J. Levy and E. Ditz, *Bull. soc. chim.*, [5] **2**, 1871 (1935); (d) J. Levy and E. Ditz, *ibid.*, [5] **2**, 1871 (1935); (e) D. Y. Curtin and P. I. Pollak, THIS JOURNAL, **73**, 992 (1951).

(9) P. I. Pollak and D. Y. Curtin, *ibid.*, **72**, 961 (1950).

(10) D. Y. Curtin and P. I. Pollak, *ibid.*, **73**, 3453 (1951).

(11) (a) The yields reported are from P. I. Pollak, Doctoral Dissertation, Columbia University, 1950; (b) this paper.

(12) A. McKenzie and A. D. Wood, *Ber.*, **71**, 358 (1938).

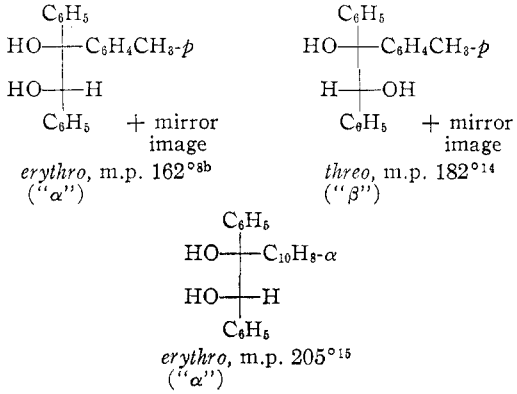
(13) A. McKenzie and F. Barrow, *J. Chem. Soc.*, **103**, 1331 (1913).

Discussion of Results

It is of interest to compare the present results with those previously reported for the reaction of acyclic aminoketones with the Grignard reagent. In a number of cases[8] only one of the two possible racemic amino alcohols has been obtained from such a reaction and recent evidence has allowed configurations to be assigned to the amino alcohols obtained.[8,9,10] The steric course of the reactions of the hydroxy- and methoxy-ketones described in the present paper is analogous to the previous results with aminoketones and in every case is that shown in Table I.

This work suggests the generalization that the reaction of an aryl Grignard reagent with a ketone with the general formula (A) may be expected to proceed stereospecifically to give (B) when Ar_1 and Ar_2 are *p*-substituted phenyl or α-naphthyl; R is phenyl or methyl; and X is NH_2, OH or CH_3O.

An immediate practical use of the generalization can be made since it provides a means for the assignment of configurations to glycols, hydroxyethers and amino alcohols similar to those above on the basis of their mode of preparation by the Grignard reaction. For example, the configurational assignments indicated below can now tentatively be made.



Although the stereochemistry of these Grignard additions may ultimately contribute to a knowledge of their mechanism it seems undesirable to speculate on this point until work bearing more directly on the mechanistic problem is available.

Experimental[16]

cis*- and *trans*-2-*p*-Anisyl-1,2-diphenylvinyl Bromide** (cis*- and *trans*-V**).—A mixture of *cis*- and *trans*-*p*-anisyl-1,2-diphenylethylene was brominated by the procedure of Koelsch.[5] From 120 g. of a mixture of isomeric olefins was obtained, after bromination and recrystallization of the crude product twice from isoöctane, 22.5 g. of impure *trans*-V, m.p. 103–111°. A sample was recrystallized repeatedly from ethanol to give the pure *trans*-isomer, m.p. 118.5–119.5° in agreement with the work of Koelsch.[5]

From the isoöctane filtrates above was obtained an isomeric bromide which had not been reported previously. Evaporation of the filtrates to dryness and recrystallization from ether and ethanol gave 6.3 g. of solid, m.p. 94.5–96.5°. Further recrystallization to constant m.p. from ethanol and ligroin gave what is probably *cis*-V, m.p. 97–98°.

Anal. Calcd. for $C_{21}H_{17}OBr$: C, 69.1; H, 4.7; Br, 21.9. Found: C, 69.1; H, 4.7; Br, 21.3.

From the various mother liquors an additional 53.3 g. of mixed isomers, m.p. 70–112°, was obtained. The total yield of *cis*- and *trans*-V was 82.1 g. (54%).

cis*- and *trans*-β-*p*-anisyl-α,β-diphenylacrylic acid** (cis*- and *trans*-II**) were obtained from the mixture of *cis*- and *trans*-V above and separated by the method of Koelsch.[5] In certain details our results differed from those of Koelsch. The *cis*-acid obtained in 11% yield, crystallized from methanol with a mole of solvent to give white needles, m.p. 179–180°.

Anal. Calcd. for $C_{22}H_{18}O_3 \cdot CH_3OH$: neut. equiv., 362. Found: neut. equiv., 367, 368.

The solvent of crystallization was readily lost even when the substance was allowed to stand at room temperature for a few hours. A sample dried at 100° *in vacuo* for four hours still melted at 179–180° but had lost the solvent of crystallization.

Anal. Calcd. for $C_{22}H_{18}O_3$: neut. equiv., 330. Found: neut. equiv., 333.

trans-II was obtained in 6% yield and like its isomer crystallized with a mole of methanol of crystallization.

Anal. Calcd. for $C_{22}H_{18}O_3 \cdot CH_3OH$: neut. equiv., 362. Found: neut. equiv., 368, 366.

The solvent of crystallization was removed by heating the material *in vacuo* for four hours at 100° to give m.p. 203.5–204.5°.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 80.0; H, 5.5, neut. equiv., 330. Found: C, 80.3; H, 5.3, neut. equiv., 330.

Koelsch had reported *trans*-II only as a hemi-hydrate, m.p. 153–155°.[5]

2-Phenyl-3-anisylindone, prepared fron *trans*-II, with thionyl chloride by the method of Koelsch,[5] was obtained in 80% yield, m.p. 109–114.5°, but after recrystallization from acetic acid and from methanol melted at 121–121.5°. The m.p. previously reported[5] was 114–115°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.6; H, 5.2. Found: C, 84.9; H, 5.3.

trans*-1-*p*-Anisyl-1,2-diphenylethylene** (trans*-III**) was prepared by decarboxylation of 1.0 g. (0.0028 mole) of *trans*-II with 0.1 g. of copper chromite[17] in 18 cc. of boiling quinoline. The reaction was allowed to proceed for 20 minutes. After extraction of the quinoline with 1 *N* hydrochloric acid and of unreacted acid with 5% sodium bicarbonate the neutral fraction was further purified by chromatography on activated alumina (40% benzene and 60% ligroin). Recrystallization of the product from methanol gave 0.47 g. (0.0016 mole, 60% yield) of *trans*-III as white needles, m.p. 90–91°. No *cis*-III was isolated.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.1; H, 6.3. Found: C, 88.3; H, 6.1.

cis*-1-*p*-Anisyl-1,2-diphenylethylene** (cis*-III**).—The decarboxylation of 1 g. (0.0028 mole) of *cis*-II was carried out exactly as above. However, in this case chromatography gave three fractions. The first (0.20 g., 0.00070 mole, 25%) was *trans*-III since after recrystallization from methanol it melted at 90–91° and a mixed m.p. with *trans*-III prepared above showed no depression.

The second fraction (0.36 g., 0.00125 mole, 45%) was a viscous oily mixture which could not be crystallized. The third fraction (0.24 g., 0.00072 mole, 30%) after recrystallization from methanol melted at 58–59° and was *cis*-1-*p*-anisyl-1,2-diphenylethylene.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.1; H, 6.3. Found: C, 88.2; H, 6.5.

The olefin mixture obtained by dehydration of 1-*p*-anisyl-1,2-diphenylethanol[5] could be separated into *cis*- and *trans*-III by chromatography. The method above gave a 47% yield of *trans*-III and 35% of *cis*-II and provided the best synthetic route to these olefins.

Oxidation with Osmium Tetroxide of *cis*- and *trans*-III.—The olefin (0.50 g., 0.0017 mole) was dissolved in 15 cc. of anhydrous ether containing 0.70 cc. (0.0090 mole) of freshly distilled pyridine. To this was added a solution of 0.45 g. (0.0018 mole) of osmium tetroxide in 15 cc. of ether. After the reaction mixture had stood overnight the osmic acid complex was collected on a filter and decomposed by the procedure of Criegee[18] by shaking for 12 hours in 15 cc. of chloroform with 40 cc. of water containing 4 g. of mannitol and 0.4 g. of potassium hydroxide. Evaporation of the chloro-

(14) A. McKenzie and A. L. Kelman, *J. Chem. Soc.*, 412 (1934).

(15) A. McKenzie and R. Roger, *ibid.*, **125**, 853 (1924).

(16) All melting points are corrected. The analyses were obtained by the Clark Microanalytical Laboratories, Urbana, Illinois.

(17) H. Adkins and R. Connor, THIS JOURNAL, **53**, 1091 (1932).

(18) R. Criegee, *Ann.*, **522**, 75 (1936); R. Criegee, B. Marchand, and H. Wannowius, *ibid.*, **550**, 99 (1942).

form layer and recrystallization from ethanol gave the glycol. From *cis*-III, was obtained 0.57 g. (100%) of the crude *erythro*-glycol, m.p. 190–198.5°, which on recrystallization gave 0.37 g. (0.0012 mole, 66%), m.p. 207.5–208.5°. Additional recrystallization raised the m.p. to 209–210°. Tiffeneau[3] reported 204° for the "α-glycol." From *trans*-III, was obtained 0.56 g. (0.0017 mole, 100%) of crude *threo*-I, m.p. 147–153°. Subsequent recrystallization from ethanol gave 0.45 g. (0.0014 mole, 81%, m.p. 156.5–157.5°). The m.p. previously reported[6] for the "β-glycol" was 156°.

Addition of *p*-Anisylmagnesium Bromide to Benzoin.—The procedure of Orekhoff and Tiffeneau[3] was repeated to give 66% of *erythro*-I, m.p. 200–202°.

Reaction of Phenylmagnesium Bromide with 4-Methoxybenzoin.—The procedure previously described[3] was repeated and in our hands gave a 69% yield of *threo*-I, m.p. 153–155°.

Conversion of *cis*- and *trans*-III to an Oxide.—*cis*-III was dissolved in 15 cc. of peroxide-free dioxane, 0.44 g. (0.0052 mole) of sodium bicarbonate in 15 cc. of water was added and the solution was cooled in an ice-bath while 0.10 cc. (0.31 g., 0.0019 mole) of bromine in 10 cc. of dioxane was added over a period of one hour. The bromine color was rapidly lost. The bromohydrin was precipitated as an oil by the addition of 30 cc. of water, extracted into ether, dried, dissolved in 7 cc. of ethanol and treated with 0.40 g. (0.0071 mole) of potassium hydroxide dissolved in 8 cc. of ethanol. The oxide was precipitated after 15 minutes by pouring the solution into 20 cc. of water. Extraction with ether, drying of the ether solution and removal of the ether gave 0.52 g. of crude 1-*p*-anisyl-1,2-diphenylethylene oxide, m.p. 68–80°. Two recrystallizations from ligroin gave 0.18 g. of white needles, m.p. 92–93.5°. *trans*-III gave the same oxide when treated in this way (as shown by m.p. and mixed m.p.). The oxide decomposed when dried under reduced pressure at 50° and was therefore dried at room temperature.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.2; H, 6.1.

Reaction of the Oxide of 1-*p*-Anisyl-1,2-diphenylethylene with Benzoic Acid.—The oxide (0.95 g., 0.0031 mole) in 1 cc. of chloroform with 0.058 g. (0.00047 mole) of benzoic acid was allowed to stand at 0° for 20 hours. After extraction of excess benzoic acid with sodium bicarbonate solution and removal of the chloroform under reduced pressure the gummy product remaining was hydrolyzed directly to the glycol by treatment with 8 cc. of 9% alcoholic potassium hydroxide under reflux for 40 minutes. Addition of 40 cc. of water precipitated 0.078 g. (0.00024 mole, 78%) of crude *erythro*-I, m.p. 170–180°. Recrystallization from ethanol gave fine needles, m.p. 205.5–206.5°. A mixed m.p. with an authentic sample prepared from *cis*-III as above showed no depression.

Benzoin methyl ether, m.p. 45–48°, was prepared in 60% yield from benzoin and methyl iodide by the method of Irvine and Weir.[19]

(19) J. C. Irvine and J. Weir, *J. Chem. Soc.*, **91**, 1391 (1907).

Reaction of *p*-Anisylmagnesium Bromide with Benzoin Methyl Ether. *erythro*-1,2-Diphenyl-1-*p*-anisyl-2-methoxyethanol (*erythro*-IV).—To a solution of 4.26 g. (0.019 mole) of ketone in 75 cc. of anhydrous ether was added anisylmagnesium bromide prepared from 0.71 g. (0.029 mole) of magnesium and 5.42 g. (0.029 mole) of *p*-bromoanisole. The product was recrystallized from 30–35 cc. of 95% ethanol to give 3.96 g. (63%) of *erythro*-IV, m.p. 132.5–136°. Repeated recrystallization from ethanol gave m.p. 135.1–135.8°. None of the *threo*-isomer was obtained.

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.0; H, 6.6. Found: C, 79.1; H, 6.6.

***erythro*-IV from the Methylation of *erythro*-I.**—Potassium sand was made from 0.24 g. (0.006 mole) of potassium metal in 45 cc. of dry benzene. A suspension in anhydrous ether of 1.50 g. (0.0047 mole) of *erythro*-I described above was added. Hydrogen was evolved very slowly over a period of 2.25 hours. At the end of that time 10 g. of methyl iodide was added rapidly, the mixture stirred, refluxed for 2 hours, and left to stand overnight. Recrystallization of the product from ethanol gave 0.45 g. of starting material, m.p. 198–200°, and 0.49 g. (44.5%), of *erythro*-IV, m.p. 130–133°. A mixed m.p. with *erythro*-IV prepared by the addition of 2-anisylmagnesium bromide to benzoin methyl ether showed no depression.

Reaction of Phenylmagnesium Bromide with 4-Methoxybenzoin Methyl Ether. *threo*-IV.—4-Methoxybenzoin methyl ether was prepared from 4-methoxybenzoin (17 g., 0.070 mole) and methyl iodide in the same way as benzoin methyl ether above. The product was obtained as 13 g. of an oil which could not be induced to crystallize. It was therefore molecularly distilled and used directly. 4-Methoxybenzoin methyl ether (2.47 g., 0.0096 mole) in 50 cc. of anhydrous ether was added to a solution of phenylmagnesium bromide prepared from 0.29 g. (0.012 mole) of magnesium turnings and 1.88 g. (0.012 mole) of bromobenzene. The product consisted of 1.94 g. (60.4% based on the assumption that the oily starting ketone was pure anisoin methyl ether) of *threo*-IV, m.p. 139–142.5°. After several recrystallizations from 95% ethanol and benzene–petroleum ether, the m.p. was 143.8–144.6°.

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.0; H, 6.6. Found: C, 79.3; H, 6.5. Mixed m.p. with *erythro*-IV, m.p. 135°, was depressed to 114°.

***threo*-IV from the Methylation of *threo*-I.**—*threo*-I (5.00 g., 0.016 mole) was converted to the potassium salt with 0.63 g. (0.016 g. atom) of potassium sand and treated with 25 cc. of methyl iodide as described for the reaction of *erythro*-I. *threo*-IV (2.07 g., 39%), m.p. 136–139°, was obtained by crystallization of the crude product from ethanol. Further recrystallization from ethanol raised the m.p. to 139–140°. A mixed m.p. with *threo*-IV obtained from the Grignard reaction above was not depressed. A mixed m.p. with samples of the *erythro*-isomer were very much depressed.

URBANA, ILLINOIS RECEIVED NOVEMBER 12, 1951