

ment. The total peroxide recovery was accordingly 90%. Elimination of the sulfuric acid catalyst from the product was best effected by flash distillation as described in the next section.

When the ion exchange resin (Amberlite IR-120) was used as the catalyst, it was first converted to its acid form by the standard treatment, in a tower, with aqueous hydrochloric acid. The resin was washed with water till free of chloride ion and then with acetic acid to displace the water. The resin was employed in the acetic acid-wet form, but the quantity of resin used was based on the calculated dry resin content. At the end of the experiment the ion exchange resin was readily removed by filtration.

Flash distillation of peroxyacid solutions to eliminate sulfuric acid. A 2000-ml., round-bottomed, 3-necked flask was fitted with a dropping funnel, a thermometer, and a short offset Claisen-type distillation head that led to the side of a Friedrich condenser which in turn drained into an ice-cooled receiver. The flask was heated by a Wood's metal bath maintained at 195 to 205°, and the pressure in the system was lowered to 175 mm. The peracetic acid solution was then fed slowly through the dropping funnel at such a rate that immediate distillation took place and no significant build-up of liquid in the flask occurred. There was negligible loss of peracetic acid when distillation was carried out under these conditions. Because of the danger of a vapor-phase detonation, however, this procedure was used only for dilute (25%) peracetic acid solutions. Although no detonations were encountered in this work, safety glass shields were always placed in front of equipment in which peracetic acid solu-

tions were being distilled. Fresh stabilizer was always added to the distilled peracid since the original stabilizer remained with the residue.

Detonability of peroxyacid solutions. The explosion tests with peracid solutions were carried out behind a protective wall of steel and concrete. An open-top 14-gage stainless steel tube, 1.5 in. in diameter and 6 in. long, was mounted in a water bath. The solution to be tested (25 ml.) was poured into the tube, and a No. 6 blasting cap was submerged and centered in the liquid. When the blasting cap was set off, a bulging of the tube occurred. This increase in diameter was taken as a measure of the severity of the detonation. Control experiments carried out with acetic acid or ethyl acetate resulted in increases in diameter of about 0.12 in. at the point of maximum bulge. With detonable solutions the explosions were often severe enough to rupture the tubes.

Fig. 1. summarizes the results of detonation tests conducted with solutions of peracetic acid at various temperatures. The curves—one for acetic acid solutions and one for ethyl acetate solutions—mark the boundaries between the detonable and nondetonable regions. Explosions were more severe the deeper the point in the detonable region.

Solutions of perpropionic acid in ethyl propionate were tested at 25°, and it was shown that they were unstable to the shock and fire of No. 6 blasting caps at peracid concentrations above 60% by weight.

SOUTH CHARLESTON, W. VA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

Synthesis of Some New Triarylethylene Glycols and Attempts to Oxidize These to α -Arylbenzoins

JEROME F. EASTHAM AND DONALD J. FEENEY

Received June 2, 1958

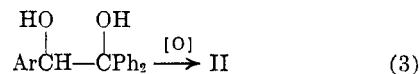
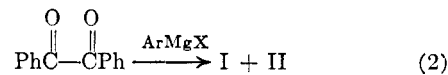
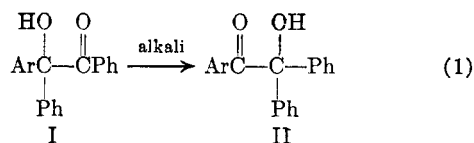
In an attempt to develop a general synthetic route to α -arylbenzoins several 1,1-diphenyl-2-arylethylene glycols have been prepared and oxidized with various reagents. This and one other route investigated for the same purpose met only partial success. In the course of the work an example of the addition of an organocadmium reagent to a carbonyl group was found and a new product from the reaction of a Grignard reagent with an aroyl cyanide was isolated.

α -Arylbenzoins (I) undergo molecular rearrangement when treated with alkali (1).^{1,2} Further, the obvious synthesis of this type of compound, inverse addition of a Grignard reagent to benzil, also may proceed with rearrangement (2).¹ Because of these rearrangements associated with the α -arylbenzoin system, a general unequivocal synthesis of the system would be desirable. Reported in this paper are two methods attempted for such a synthesis.³

(1) J. F. Eastham, J. E. Huffaker, V. F. Raaen, and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 4232 (1956).

(2) W. von E. Doering and R. S. Urban, *J. Am. Chem. Soc.*, **78**, 5938 (1956). The tentative conclusion of these authors that α -arylbenzoin rearrangement (1) occurs only when steric strain is released is incorrect. With C-14-labeled α -anisylanisoin it was shown¹ that rearrangement occurs with the only change being a mixing of the position of labeling.

(3) Previous methods of synthesis, other than that of equation 2, have yielded only three crystalline α -arylbenzoins. H. Biltz [*Ber.*, **32**, 655 (1899)] obtained α -phenyl-



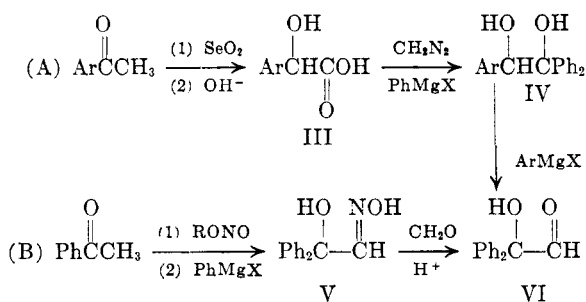
The first method attempted (Equation 3) was oxidation of α -aryldihydrobenzoins, *i.e.*, 1,1,2-tri-benzoin by oxidation of α -phenyldeoxybenzoin with nitric acid; W. E. Bachmann [*J. Am. Chem. Soc.*, **54**, 2112 (1932)] obtained 2-methyl- α -phenylbenzoin by addition of *o*-tolylmagnesium bromide to methyl benzilate; and D. Y. Curtin and S. Leskowitz [*J. Am. Chem. Soc.*, **73**, 2633 (1951)] obtained α -benzhydrylbenzoin by a molecular rearrangement of benzhydryl desyl ether. None of these methods of synthesis seems general.

TABLE I
 1,1-DIPHENYL-2-ARYLETHYLENE GLYCOLS (IV) PREPARED

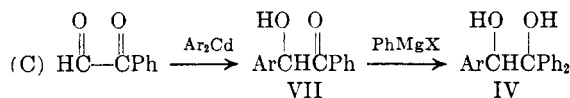
Aryl Group in Glycol IV	Glycol M.P.	Starting Material	Yield, %	Calcd. for	Analysis			
					Carbon, %		Hydrogen, %	
					Calcd.	Found	Calcd.	Found
<i>o</i> -Tolyl ^a	126–127°	III	61					
<i>m</i> -Tolyl	140.5–141°	III	54	C ₂₁ H ₂₀ O ₂	82.86	82.72	6.62	6.56
<i>p</i> -Tolyl	194.5–195°	III	55	C ₂₁ H ₂₀ O ₂	82.86	82.96	6.62	8.85
<i>o</i> -Anisyl	134–134.5°	V	58	C ₂₁ H ₂₀ O ₃	78.72	78.90	6.29	6.39
<i>m</i> -Anisyl	150–151°	V	51	C ₂₁ H ₂₀ O ₃	78.72	78.80	6.29	6.24
<i>p</i> -Anisyl ^b	200–202°	V	63					
2,5-Xylyl	129–129.5°	V	37	C ₂₂ H ₂₂ O ₂	82.98	82.70	6.96	6.88

^a Previously prepared by R. Roger and F. C. Harper, *Rec. trav. chim.*, **56**, 202 (1937). ^b Previously prepared by J. E. Huffaker, Master of Science thesis, University of Tennessee, August, 1956.

arylethylene glycols. Since we were particularly interested in the benzoin (II) produced by rearrangement in equation 2, the glycols synthesized were 1,1-diphenyl-2-arylethylene glycols (IV). Glycols of this type, reported in Table I, were successfully prepared by two conventional routes: (A) through addition of excess phenyl Grignard reagent to methyl esters of substituted mandelic acids (III), and (B) through addition of aryl Grignard reagents to benzilaldehyde. By the first method (A) it was not necessary to isolate the methyl esters, produced with diazomethane, and by the latter method (B) it was not necessary to isolate the benzilaldehyde (VI) produced from its oxime (V). The structures of the new glycols in Table I were proved by oxidative cleavage of the glycols to the expected benzophenone and substituted benzoic acids. Typical details of the routes (A and B) and the cleavages are given in the Experimental section.



A third route (C) briefly considered for synthesis of glycols IV was addition of phenyl Grignard reagent to unsymmetrical benzoin (VII). Unfortunately benzoin like VII are not readily available;

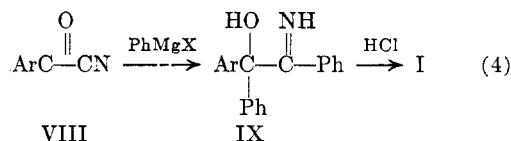


they are usually unstable with respect to isomers with carbonyl adjacent to the substituted benzene ring.⁴ One attempt made to develop a quick general synthesis of these "unstable" benzoin was by addition of a diarylcadmium reagent to phenylgly-

oxal. Although this attempt was not generally successful, benzoin itself was produced by reaction of phenylglyoxal with diphenylcadmium. This constitutes one of the rare instances of addition by an organocadmium reagent to a carbonyl group.

With 1,1,2-triphenylethylene glycol as a model for the oxidation in Equation 3, several techniques were investigated; oxidizing agents tried included nitric acid, chromic acid, manganese dioxide, and selenium dioxide. Only with the latter reagent could the desired reaction (3) be satisfactorily effected. Treatment of 1,1,2-triphenylethylene glycol with molten selenium dioxide (no solvent) gave the crystalline α -phenylbenzoin in a yield of 65%. In a similar manner oxidation of 1,1-diphenyl-2-*o*-tolylethylene glycol yielded α -phenyl-2-methylbenzoin in a yield of 70%.

Application of the same technique to various other triarylethylene glycols in Table I resulted in oils which could not be induced to crystallize. Satisfactory elemental analyses could be obtained from these oils after their distillation. However, we do not feel that these noncrystalline products should be reported as new, pure α -arylbenzoin; very likely they are mixtures of isomers like I and II.⁵



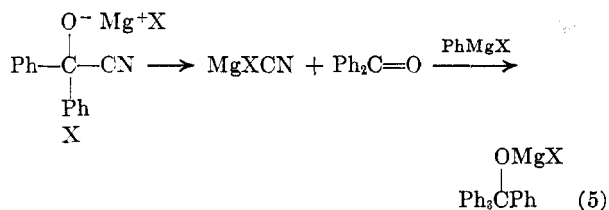
The second method investigated for preparation of α -arylbenzoin involved addition of excess phenyl Grignard reagent to an aroyl cyanide (VIII). Since this preparation (4) should lead through the ketimine IX⁶ it was hoped that side products and

(5) High purity or seed crystals of the α -arylbenzoin seem to be required for their crystallization. The few known examples of the compounds are remarkably low melting for their molecular weight and polar functional groups; for example, both α -phenyl- and α -benzhydryl-benzoin melt at 87°. Also, a small amount of impurity causes a large melting point depression with this type of compound. Even pure α -*o*-tolylbenzoin, m.p. 82°, is an exceedingly tedious compound to recrystallize.

(6) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954, p. 767.

(4) W. S. Ide and J. S. Buch, *Org. Reactions*, **IV**, 269–304 (1948).

starting material could be easily removed by extraction of IX into aqueous acid for its hydrolysis to the desired product (I).⁵ Starting with benzoyl cyanide (VIII) the technique works for preparation of α -phenylbenzoin, albeit in only 5% yield. The principal product in the reaction is triphenylmethanol, a fact noted in previous studies of the reaction between benzoyl cyanide and phenyl Grignard reagent.⁷ These previous studies had failed however to find the α -phenylbenzoin produced, presumably because the basic character of the intermediary ketimine was not utilized in its isolation.



Triphenylmethanol arises most probably from those benzoyl cyanide molecules which react first at the carbonyl group, giving an intermediate like X which decomposes to benzophenone (Equation 5). If initial addition to the carbonyl group could be slowed, then some addition might occur first at the cyanide group, resulting in a better yield of the α -arylbenzoin. On the basis of this reasoning *o*-toluyl cyanide was next tried with excess phenyl Grignard reagent. α -*o*-Tolylbenzoin was produced, and the yield of the benzoin was better, but still was only 8%. Because of the poor yields from this reaction (4) it was not further studied.

EXPERIMENTAL⁸

Preparation of mandelic acids (III). The technique for this preparation is illustrated with *m*-methylmandelic acid. A solution of 24 g. of selenium dioxide, 5 ml. of water, 20 ml. of dioxane, and 29 g. of *m*-methylacetophenone (b.p. 107–109°/12 mm., prepared by reaction of *m*-toluyl chloride with dimethylcadmium) was refluxed for 4 hr. The supernatant solution was decanted from precipitated selenium and the solvents were distilled. The residue was triturated with ether which was in turn filtered, washed with dilute base, dried, and evaporated. The residue was distilled to yield 20 g. (62%) of *m*-tolylglyoxal, b.p. 88–90°/0.1 mm.

A solution of 20 g. of the *m*-tolylglyoxal in 30 ml. of 95% ethanol was added dropwise to a vigorously stirred solution of 20 g. of sodium hydroxide in 180 ml. of water maintained at 60°. The temperature of the reaction mixture was maintained at 60–65° for 2 additional hours of stirring. The basic solution was cooled, washed with ether, acidified with hydrochloric acid, and then continuously extracted with ether for 48 hr. The ether was evaporated and the residual material recrystallized from benzene to give 10.1 g. (45%) of *m*-methylmandelic acid, m.p. 83–84° (lit.⁹ value 84°).

Preparation A of 1,1-diphenyl-2-arylethylene glycols. The technique for this preparation is illustrated with 1,1-di-

phenyl-2-*m*-tolylethylene glycol. A solution of 4.4 g. of *m*-methylmandelic acid and excess diazomethane in 100 ml. of ether was maintained in an ice bath for 1 hr. The solution was allowed to warm to room temperature, extracted with dilute base, carefully dried, and distilled to one half its volume. The solution was then added to the Grignard reagent prepared from 13.8 g. of bromobenzene and 2.2 g. of magnesium in 50 ml. of ether. After 1 hr. of reflux the reaction mixture was treated with dilute hydrochloric acid and worked up in the usual manner. The crude product was recrystallized three times from 95% ethanol to give 2.6 g. (54%) of 1,1-diphenyl-2-*m*-tolylethylene glycol, m.p. 140.5–141°. (See Table I).

Benzaldehyde oxime (V). The procedure of Orekhoff and Tiffeneau¹⁰ was followed as closely as possible. To the Grignard reagent prepared from 196 g. of bromobenzenes and 31 g. of magnesium in 1.3 l. of ether there was added in small portions 30 g. of powdered phenylglyoxal aldoxime (m.p. 123–127°, prepared by the method of Claisen and Manasse¹¹). The reaction mixture was refluxed for 2 hr. and treated with dilute aqueous acetic acid. The ethereal solution was separated, washed with aqueous sodium bicarbonate, dried, and evaporated at room temperature under reduced pressure. The waxy residue was recrystallized from benzene to yield 31 g. (66%) of benzaldehyde oxime, m.p. 120–121° (lit.¹¹ value 121°).

Preparation B of 1,1-diphenyl-2-arylethylene glycols. The above oxime (V) was hydrolyzed to benzaldehyde by the procedure of Freon.¹² A mixture of 18 g. of V, 15 ml. of 12*N* hydrochloric acid, and 15 ml. of 30% aqueous formaldehyde was stirred and maintained at 60–70° for 2 hr. After the mixture had cooled the oily layer was separated and the aqueous layer was extracted with ether. This ether was combined with the oil, washed with aqueous sodium bicarbonate, and carefully dried. Without further purification aliquots of this ethereal solution were treated with Grignard reagents. The technique is illustrated with the preparation of 1,1-diphenyl-2-*m*-anisylethylene glycol.

One eighth (15 ml.) of the above ethereal solution of benzaldehyde was added to the Grignard reagent prepared from 1.2 g. of magnesium and 9.3 g. of *m*-bromoanisole in 50 ml. of ether. The reaction mixture was refluxed for 30 min., treated with dilute hydrochloric acid, and worked up in the usual manner. The crude product was triturated with cold hexane and recrystallized twice from hexane-benzene to yield 1.7 g. (51% based on V) of 1,1-diphenyl-2-*m*-anisylethylene glycol, m.p. 150–151°. (See Table I.)

Addition of diphenylcadmium to phenylglyoxal. To the Grignard reagent prepared from 1.2 g. of magnesium and 7.1 g. of bromobenzene in 45 ml. of ether was added 4.2 g. of anhydrous cadmium chloride. The ether solvent was removed from the mixture by distillation and replaced with 50 ml. of benzene. To the benzene solution was added 5.0 g. of dry phenylglyoxal¹³ in 10 ml. of benzene. The reaction mixture was refluxed for 30 min., treated with saturated aqueous ammonium chloride, and worked up in the usual manner. The crude product was recrystallized from absolute ethanol to give 4.0 g. (51%) of benzoin, m.p. 133–134° with or without admixture of authentic benzoin.

Oxidative cleavage of 1,1-diphenyl-2-arylethylene glycols. The technique is illustrated with 1,1-diphenyl-2-*m*-tolylethylene glycol. A solution of 0.1 g. of the glycol, 0.05 g. of chromium trioxide, 2 drops of water, and 4 ml. of glacial acetic acid was maintained at 15° for 1 hr., diluted with ether, extracted with aqueous alkali, dried and evaporated.

(10) A. Orekhoff and M. Tiffeneau, *Bull. soc. chim. France*, **41**, 841 (1927).

(11) L. Claisen and O. Manasse, *Ber.*, **20**, 2194 (1882).

(12) P. Freon, *Ann. chim. (Paris)*, **11**, 507 (1939).

(13) The phenylglyoxal was dried by adding a small amount of benzene to it and removing the benzene by distillation at atmospheric pressure. The residual phenylglyoxal was then distilled, b.p. 93–96°/25 mm.

(7) R. Adams, H. B. Bramlet, and F. H. Tendick, *J. Am. Chem. Soc.*, **42**, 2369 (1920); A. De Coster, *Bull. soc. chim. Belg.*, **35**, 235 (1926).

(8) Melting points are reported uncorrected. Analyses were performed by Weiler and Strauss, Oxford, England.

(9) E. Bonnemann, *Ber.*, **17**, 1469 (1884).

From the residue the 2,4-dinitrophenylhydrazone (m.p. 238–239°) of benzophenone was prepared. From the aqueous alkali *m*-toluic acid (m.p. 111–112°) was precipitated.

Oxidation of triarylethylene glycols with selenium dioxide. The following technique yielded a crystalline benzoin (II) from triphenylethylene glycol and from 1,1-diphenyl-2-*o*-tolylethylene glycol, but not from any of the other glycols in Table I. A molten mixture of 5 g. of 1,1-diphenyl-2-*o*-tolylethylene glycol and 1.5 g. of selenium dioxide was stirred and maintained at a temperature of 200° for 5 min. The cooled mixture was triturated with ether which was in turn washed with aqueous sodium bicarbonate, dried, and evaporated. The residue was recrystallized twice from hexane-benzene to give 3.2 g. (65%) of α -phenyl-2-methylbenzoin, m.p. 116–117° with or without admixture of authentic material.¹

α -Phenylbenzoin from benzoyl cyanide. To the Grignard reagent prepared from 94 g. of bromobenzene and 1.5 g. of magnesium in 75 ml. of ether there was added dropwise over a period of 30 min. a solution of 2.6 g. of benzoyl cyanide¹⁴ in 40 ml. of ether. A granular precipitate appeared in the stirred reaction mixture as rapidly as the cyanide was added. The reaction mixture was poured into a vigorously

stirred mixture of ice and dilute hydrochloric acid contained in a separatory funnel. As soon as the layers separated the aqueous layer was quickly drawn off and allowed to stand at room temperature overnight. The ether layer was worked up in the usual manner to yield 4.3 g. (85%) of triphenylmethanol, m.p. 162–163°. The aqueous layer, after standing overnight, was extracted with ether which was in turn washed, dried, and evaporated. The residue was recrystallized from ligroin to give 0.27 g. (5%) of α -phenylbenzoin, m.p. 87–88° (lit.¹⁵ value 87–88°).

*α -*o*-Tolylbenzoin.* The procedure employed was that described above. After reaction between Grignard reagent (from 18.2 g. of bromobenzene and 2.9 g. of magnesium) and *o*-toluyl cyanide (4.2 g., b.p. 202–204°/750 mm., prepared from *o*-toluyl chloride as described for benzoyl cyanide¹⁴) the reaction mixture was distributed between ether and aqueous acid. The ether layer was discarded and the aqueous acid, after standing overnight, worked up as before. Recrystallization of the crude product gave 0.70 g. (8%) of α -*o*-tolylbenzoin, m.p. 81–82° with or without admixed authentic material.¹

KNOXVILLE, TENN.

(14) T. S. Oakwood and C. A. Weisgerber, *Org. Syntheses, Coll. Vol. III*, 114 (1955).

(15) S. F. Acree, *Ber.*, **37**, 2753 (1904).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Base-Catalyzed Alkylations with Alcohols. IV

STEPHEN S. HIRSCH,¹ DONALD H. LORENZ,¹ AND ERNEST I. BECKER²

Received June 9, 1958

Refluxing a mixture of indene with sodium benzylate in benzyl alcohol produced dibenzylindene. With added Raney nickel 3-benzyl-1-benzylideneindene was obtained. A third hydrocarbon, believed to be 1-benzylideneindane, was also isolated.

Fluorene was alkylated with 2-diethylamino- and 2-dimethylaminoethanol to give the corresponding 9-(2-dialkylaminoethyl)fluorenes. With ethoxyethanol 9-(2-ethoxyethyl)fluorene was obtained.

The purpose of the present investigation was to determine whether indene, with two potentially active positions, would be alkylated twice with benzyl alcohol and sodium benzylate, and to determine whether fluorene could be alkylated with substituted alcohols as extensions of previous work in this field.^{3,4}

The first attempt to alkylate indene was carried out with *n*-propyl alcohol and sodium *n*-propylate in a reaction bomb at 210°, or under reflux, but no isolable product was obtained. However, upon employing benzyl alcohol and sodium benzylate, which has been exploited successfully by Sprinzak and his co-workers,⁵ with or without diisopropylbenzene as a solvent, dibenzylindene (I), m.p. 60.3–62.0°, was obtained as the major product. When a mixture of indene with a small amount of

sodium benzylate in a large excess of benzyl alcohol in the presence of Raney nickel was refluxed with or without diisopropylbenzene as a solvent 3-benzyl-1-benzylideneindene (II), a yellow solid, m.p. 137.4–138.4°, was obtained.

In the first reaction, using UOP nickel instead of Raney nickel, a small amount of a white solid (III), believed to be 1-benzylideneindane, m.p. 73.4–74.4°, was isolated. The proofs of structure for the three products follow.

Dibenzylindene. The melting point and the melting point of the dibromo derivative agreed with the reported values.⁶ Additional information was added when the molecular weight and the ultimate analysis agreed with those expected for the hydrocarbon. The nuclear magnetic resonance spectrum was also confirmatory: Band 1, 90 cycles on the low field side of water (aromatic CH); Band 2, 49 cycles on the low field side of water (=CH); Band 3, 43 cycles on the high field side of water (=C—CH₂—C=); Band 4, peaks at 47 and 54 cycles on the high field side of water (H in the 1-position); Band 5, peaks at 72, 76 and 83 cycles

(1) From the B.S. theses of S. S. Hirsch and D. H. Lorenz, Polytechnic Institute of Brooklyn, 1958.

(2) To whom inquiries should be sent.

(3) M. Avramoff and Y. Sprinzak, *J. Org. Chem.*, **22**, 571 (1957).

(4) I. D. Rubin and E. I. Becker, *J. Org. Chem.*, **22**, 1623 (1957).

(5) See footnote 3 and papers cited therein.

(6) J. Thiele and A. Buhner, *Ann.*, **347**, 249 (1906).