78° and then under reflux for 18 hr. The mixture was then poured rapidly on pulverized Dry Ice which had been spread evenly on the bottom of a 4-l. beaker. The reaction mixture was allowed to stand overnight and decomposed with cold hydrochloric acid. The organic layer was washed with water and extracted with three 100-ml. portions of 5% sodium hydroxide. The basic extract was diluted to 800 ml. and then heated on a steam bath. The colorless β,β-diphenylpropiophenone that separated was collected by filtration, yield 4.1 g. When the filtrate was acidified with hydrochloric acid, a copious, colorless precipitate appeared. The acidified mixture was heated to 90°, and 0.9 g. of undissolved solid was collected by filtration. The solid was dissolved in hot ethanol, and the resulting solution filtered to remove insoluble impurities. When cooled the solution deposited the pure acid as a colorless solid, yield 0.4 g. (4%), m.p. 215–216°.

Anal. Calcd. for $C_{28}H_{24}O_3$: C, 82.33; H, 5.92. Found: C, 82.51; H, 6.17.

The acid was made also from β,β-diphenyl-α-bromopropiophenone by way of benzhydrylbenzoylacetic acid. The bromo ketone (10 g., 0.027 mole) in 30 ml. of ether was added to a 0.087-mole portion of phenylmagnesium bromide solution in ether. The reaction mixture was stirred for 2 hr. and then poured into a slurry of Dry Ice in ether. A colorless salt, collected by filtration, was washed with two 100-ml. portions of ether and decomposed with dilute hydrochloric acid by prolonged shaking. The product was extracted with ether, and the organic layer was washed with water and dried. After evaporation of the ether a colorless solid remained. Two recrystallizations from an acetone–petroleum ether mixture gave the benzhydrylbenzoylacetic acid as short, white needles, m.p. 127–128°, with decomposition, yield 5.8 g. (60%).

To a cooled phenylmagnesium bromide solution containing 0.03 mole of reagent was added rapidly 3.3 g. (0.01 mole) of α-benzhydrylbenzoylacetic acid in 30 ml. of ether. A colorless precipitate appeared immediately in the reaction mixture, which was then stirred for 4 hr. Nearly 2 g. of β,β-diphenylpropiophenone was recovered, and 0.42 g. (10%) of 2-benzhydryl-3-hydroxy-3,3-diphenylpropionic acid was obtained. A mixed melting point with an authentic sample of the acid did not show a depression.

The acid (0.8 g.) was dissolved in 10 ml. of alcohol and to this solution was added 0.5 ml. of concentrated hydrochloric acid. The mixture was heated on a steam bath for 15 min. and stored overnight in a refrigerator. The product (0.65 g.) was recrystallized from alcohol, m.p. 124–126°. A mixed melting point determination and the infrared spectral data indicate that the product is 1,1,3,3-tetraphenylpropene.

Methyl 2-benzhydryl-3-hydroxy-3,3-diphenylpropionate. To a solution of 0.4 g. (0.001 mole) of 2-benzhydryl-3-hydroxy-3,3-diphenylpropionic acid in 30 ml. of an ether-benzene mixture was added an ether solution of diazomethane prepared from 1 g. of *N*-nitrosomethylurea.[10] The solution was kept in an ice bath for 1 hr. and then allowed to warm to room temperature. After 8 hr. it had turned nearly colorless, and the solvent was evaporated. The ester, isolated as a colorless solid (0.4 g.), was recrystallized from ethanol, m.p. 170–171°.

Anal. Calcd. for $C_{29}H_{26}O_3$: C, 82.44; H, 6.20. Found: C, 82.02; H, 6.21.

A solution of 0.4 g. of the ester in 15 ml. of acetic anhydride was heated under reflux for 12 hr.; 0.3 g. of starting material was recovered.

Attempted hydrogenolysis of 2-benzhydryl-3-hydroxy-3,3-diphenylpropionic acid. The acid in absolute ethanol was treated with hydrogen gas with Raney nickel as a catalyst at a pressure of 50 atm. and 100° for 4 hr. The product, a colorless oil, could not be induced to crystallize. Its infrared spectrum showed a weak carbonyl band. It was concluded that fragmentation of the acid had occurred.

To a solution of the acid (0.2 g., 0.0005 mole) in 35 ml. of ethanol was added 10% palladium-on-charcoal as a catalyst. The acid failed to take up hydrogen over a period of 8 hr. and was recovered quantitatively. Hydrogenolysis also failed to occur with platinum oxide as a catalyst and at a pressure of 4 atm. of hydrogen.

URBANA, ILL.

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[10] F. Arndt, *Org. Syntheses*, **Coll. Vol. II**, 165 (1943).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

Reactions of *trans*-α-Phenylchalcone Oxides with Phenylmagnesium Bromide and Phenyllithium[1]

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The reactions of phenylmagnesium bromide and phenyllithium with *trans*-α-phenylchalcone oxide and two related *trans*-α,-β-epoxyketones have been investigated. The phenyl substituent in the α- position of the chalcone oxide bestowed an added stability on the primary addition products and permitted the isolation of the α,β-epoxy alcohols when excess organometallic reagent was used at room temperature. When the α,β-epoxy alcohols were forced to cleave under the influence of acid or organometallic reagent, the manner of cleavage depended upon the substitution in the molecule and on the reagent used.

Previously studied Grignard reactions of α,β-epoxy ketones had generally been observed to yield epoxy alcoholates which readily underwent cleavage.[3] Since the observed cleavage took place between the oxirane ring and the alcoholic side chain as shown in Fig. 1, path A, it was decided to investigate the effect of an α-phenyl substituent on the course of the reaction. One equivalent of phenylmagnesium bromide reacted with *trans*-α,β-diphenylacrylophenone oxide (I) at room temperature to form an ether-insoluble complex

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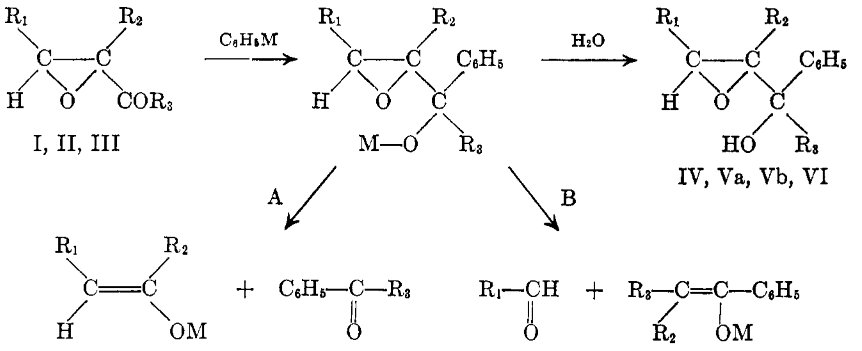
[1] Presented at the national meetings of the American Chemical Society in Miami in April 1957 and in New York in September 1957.

[2] Taken from the thesis presented to Fordham University in partial fulfillment for the Ph.D. degree by S. S. F. Dilgen, 1959.

[3] (a) N. G. Gaylord and E. I. Becker, *Chem. Revs.* **49**, 413 (1951). (b) E. P. Kohler and C. L. Bickel, *J. Am. Chem. Soc.*, **57**, 1099 (1935). (c) E. P. Kohler, N. K. Richtmyer, and W. F. Hester, *J. Am. Chem. Soc.*, **53**, 205 (1931). (d) C. L. Bickel, *J. Am. Chem. Soc.*, **59**, 325 (1937).

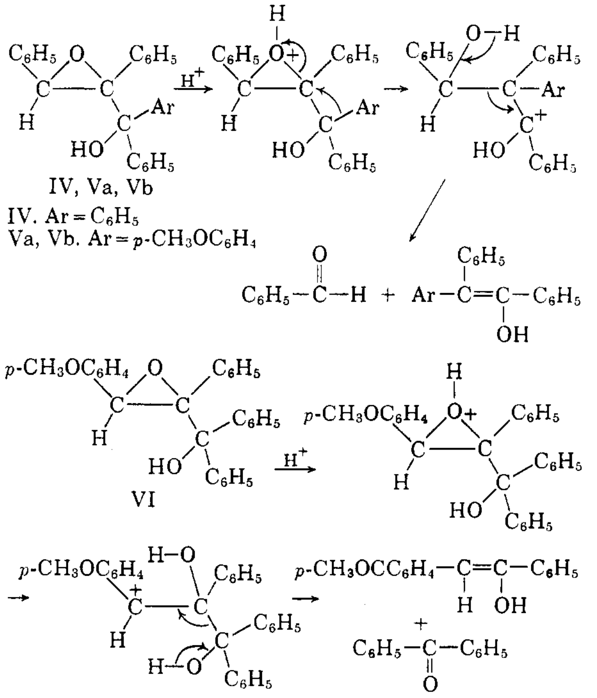


	R_1	R_2	R_3	Type of Cleavage M = MgBr	 M = Li
	C_6H_5	H	C_6H_5	A[3c]	A[3b]
I. IV	C_6H_5	C_6H_5	C_6H_5	B	A
II. Va, Vb	C_6H_5	C_6H_5	p-$CH_3OC_6H_4$	B	—
III. VI	p-$CH_3OC_6H_4$	C_6H_5	C_6H_5	—	A

Figure 1

which upon hydrolysis regenerated the starting epoxy ketone. The same result was obtained with *trans*-α,β-diphenyl-*p*-methoxyacrylophenone oxide (II). Prolonged refluxing of the reaction mixtures before hydrolysis yielded not only the unchanged epoxy ketones but also bromohydrins resulting from the addition of hydrogen bromide to the epoxide ring. Each of the bromohydrins underwent ring closure with base to reform the epoxy ketone from which it had been obtained. The failure of a compound to undergo addition when treated with one equivalent of Grignard reagent has been previously observed with both ketones and epoxides and is attributed to complex formation.[4] The formation of a halohydrin in the reaction of an epoxide with a Grignard reagent is not unusual, although an organometallic reagent is ordinarily more reactive towards a carbonyl group than towards the epoxide ring.[3a,4a]

When four equivalents of phenylmagnesium bromide reacted with the *trans*-epoxy ketones at room temperature, addition to the carbonyl group took place to yield the *trans*-α,β-epoxy alcohols. I yielded *trans*-2,3-epoxy-1,1,2,3-tetraphenyl-1-propanol (IV); II yielded the diastereomeric *trans*-1-(*p*-anisyl)-2,3-epoxy-1,2,3-triphenyl-1-propanols (Va and Vb); and *trans*-β-(*p*-anisyl)-α-phenylacrylophenone oxide; III yielded *trans*-3-(*p*-anisyl)-2,3-epoxy-1,2,3-triphenyl-1-propanol (VI). The structures assigned to these products are supported by analyses, infrared spectra, and active hydrogen determination of IV and Va. Addition to the carbonyl group is confirmed by the reaction of I with anisylmagnesium bromide to give the same two compounds, Va and Vb, as had been obtained from the reaction of II with phenylmagnesium bromide. Acidic cleavage further confirms the assigned structures. When IV, Va, and Vb reacted with hydrogen chloride in glacial acetic acid, benzaldehyde was obtained from the three reactions with α-phenyldesoxybenzoin from IV and α-anisyldesoxybenzoin from Va and Vb. In contrast to this, the action of hydrogen chloride in glacial acetic acid on VI yielded benzophenone and *p*-methoxybenzyl phenyl ketone.[5] The paths proposed for the two types of acidic cleavage that have



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(4) (a) M. S. Kharasch and Otto Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, New York, 1954, p. 139; p. 961. (b) C. G. Swain and H. B. Boyles, *J. Am. Chem. Soc.*, **73**, 871 (1951). (c) G. F. Wright, *Steric Effects in Organic Chemistry*, M. S. Newman, ed., J. Wiley, New York, 1956, Chap. 8, pp. 395–424. (d) N. H. Cromwell, J. H. Anglin, Jr., F. W. Olsen, and N. C. Barker, *J. Am. Chem. Soc.*, **73**, 2805 (1951).

(5) A review of previously observed cleavages of α,β-epoxy alcohols and α,β-epoxy ketones was prepared by M. Darmon, *Bull. soc. chim. France*, D25 (1953).

been observed suggest that the factors determining the course of the reaction are anchimeric assistance by the migrating aryl groups in IV and V to electron withdrawal at the α-carbon and electromeric assistance by the *p*-anisyl group to electron withdrawal at the β-carbon of VI. The assignment of configuration to the α,β-epoxyalcohols is based on the constancy of configuration around the epoxide ring during carbonyl addition.

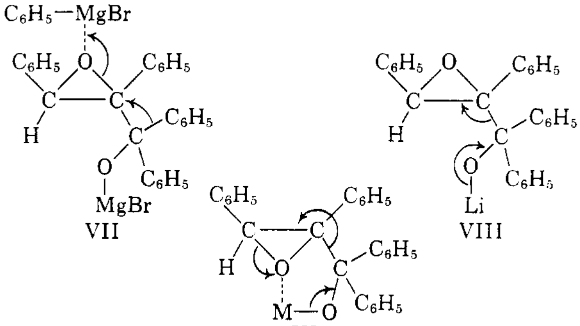
The obtainment of the epoxy alcohols at room temperature in the above reactions was in marked contrast to the cleavage products which previous investigators had usually obtained from chalcone oxides without the α-phenyl substituent. The refluxing of I with an excess of ethereal phenylmagnesium bromide effected the partial cleavage of the epoxy alcoholate according to Figure I, path B to yield small amounts of the cleavage products, α-phenyldesoxybenzoin and benzhydrol, as well as the epoxy alcohol. When II was refluxed with excess phenylmagnesium bromide in ethereal solution, the cleavage products were α-anisyldesoxybenzoin and benzhydrol. The latter product results from the reaction of the initially formed benzaldehyde with the excess reagent.

When one equivalent of phenyllithium reacted with I at room temperature, only the starting epoxy ketone was obtained upon hydrolysis. With two equivalents of the lithium reagent, an addition took place to yield IV, the same product as had been obtained with the Grignard reagent. From the reaction of II with two equivalents of phenyllithium at room temperature only one of the two possible diastereomers was isolated, *viz*, Vb, that which had been obtained in lower yield in the Grignard reaction. The contrast between the two reagents was more marked in the reactions of III. Instead of the α,β-epoxy alcohol, phenyllithium gave *p*-methoxybenzyl phenyl ketone and benzophenone, according to path A.

When an etheral solution of four equivalents of phenyllithium was refluxed for four hours with I, the products, triphenylcarbinol and desoxybenzoin, indicated that the initially formed lithium epoxy alcoholate underwent cleavage according to path A, different from that observed under forcing conditions with the Grignard reagent. A third product from this reaction was an unidentified carbonyl compound which is probably a tetraphenylpropiophenone. The same three products were obtained when the α,β-epoxy alcohol, IV, reacted with phenyllithium at reflux temperature. When II reacted with phenyllithium at reflux temperature the yield of the addition product was reduced to 22% but other products were not isolated from the oily residue.

A comparison of the organometallic reactions of the chalcone oxides presented in this paper with those previously reported in the literature[3,4a,5] shows that the α-phenyl substituent has had various effects on the course of the reactions. In the majority of the reactions it stabilized the intermediate epoxy alcoholates preventing ready cleavage.[6] In certain compounds it changed the direction of ring opening when this did occur under forcing conditions. It also appears to differentiate between the magnesium and lithium reagents since each causes a different type of cleavage of I.

Stabilization of the three-membered ring by the α-aryl substituent may account for the stability of the epoxy alcoholates.[7] The ring opening of the magnesium alcoholates of IV and V at the tertiary α-carbon, rather than at the secondary β-carbon would be expected if the impetus for the reaction is the pull of the positive pole at the complexed oxirane oxygen VII causing ring opening at whichever carbon the assistance is greater. This is supported by the hydrogen chloride cleavage of the oxanols which, in each case, follows the same path as cleavage by the Grignard reagent. In the contrasting type of cleavage of IV effected by phenyllithium, the impetus for the reaction may come from the electron release by the carbinolate oxygen VIII, which may be the controlling factor in this case due to the more polar nature of the oxygen-lithium bond.[8]



VII

VIII

IX

An alternate explanation for the observed differences in the cleavages effected by the two reagents may be the five-membered chelate IX, which various authors have proposed as taking part in the cleavage by organometallic reagents which occurs between the carbinolate carbon and the α-carbon.[9] When the chelate forms, path A cleavage products are obtained, but the presence of the α-substituent may prevent the formation of the chelate, thereby changing the mechanism of the

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(6) A recent example of the stability of an α-substituted epoxy alcoholate is found in N. H. Cromwell and R. E. Bambury, *J. Org. Chem.*, **26**, 997 (1961).

(7) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952); G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, and W. D. Gwinn, *J. Chem. Phys.* **19**, 676 (1951).

(8) J. P. Freeman and M. F. Hawthorne, *J. Am. Chem. Soc.* **78**, 3366 (1956).

(9) (a) T. A. Geissman and V. Tulagin, *J. Am. Chem. Soc.*, **63**, 3352 (1941). (b) T. A. Geissman and L. Morris, *J. Am. Chem. Soc.*, **66**, 716 (1944). (c) H. H. Wasserman, "Steric Effects in Organic Chemistry," M. S. Newman, ed. J. Wiley, New York, 1956, Chap. 7, p. 373.

reaction and, in certain cases, the products. The different steric requirements of the lithium reagent may permit the formation of the chelate even with compounds bearing the α-substituent or the more polar nature of the lithium reagent yields path A cleavage regardless of chelate formation. This investigation is presently being extended to the study of the organometallic reactions of various other α,β-epoxy ketones in an effort better to understand the factors which control the course of the reactions.

EXPERIMENTAL[10]

trans-α,β-Diphenylacrylophenone oxide (I). Twenty grams (0.07 mole) of *trans*-α,β-diphenylacrylophenone prepared by the procedure of Kohler and Nygaard[11] was suspended in 500 ml. of methanol to which 60 ml. of a 30% solution of hydrogen peroxide and 40 ml. of 10% sodium hydroxide were added. The mixture was heated to 60° and stirred at this temperature for 20 min.[12] Ice water was added to the partially cooled solution and the white precipitate was collected on a Büchner funnel, washed with water, and recrystallized from a methanol–water mixture to yield 14.5 g. (60%) of the oxide I, m.p. 82–83°. (lit.,[13] 82.5–83.5) The infrared spectrum determined in chloroform solution exhibited a band in the carbonyl region at 5.92 μ.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.83; H, 4.94.

trans-α,β-Diphenyl-p-methoxyacrylophenone. A mixture of 121 g. (0.53 mole) of anisyl benzyl ketone[14] and 106 g. (1 mole) of freshly distilled benzaldehyde was cooled in an ice bath while dry hydrogen chloride was run in during 6 hr. The mixture, on standing overnight, solidified. The orange solid was broken up under alcohol, washed with alcohol and with ether, and dried. In this way, 130 g. of crude hydrogen chloride addition product was obtained. This material was refluxed in 500 ml. of methanol with 114 g. of fused potassium acetate and 34 g. of anhydrous sodium carbonate for 5 hr. The supernatant liquid was decanted through a filter from the residue of oil and solid which remained in the flask. The residue was dissolved in ether, washed well with water to remove the inorganic salts and filtered to remove an insoluble residue. The ether solution was dried, evaporated, and the residue crystallized from methanol to yield α,β-diphenyl-p-methoxyacrylophenone, m.p. 90–91° (lit.,[15] m.p. 90–91°). The crystalline material which precipitated from the original methanol filtrate was collected and recrystallized to give more of the same compound. The total combined yield was 72 g. (43%). On standing, material which melted broadly at about 70° precipitated from the methanol filtrate. When this was recrystallized from an acetone–water mixture, two types of crystals formed, one bulky and rhombic, the other fine and monoclinic. Both melted at 92–93° upon recrystallization, but the mixed melting point was depressed to 70°. The mixed melting point of one of these compounds with the material from the first fractions was depressed and the other was not. The infrared spectra of the compounds were very similar. The material which had been obtained in the larger yield was assigned the trans configuration of the basis of its ease of oxidation with alkaline hydrogen peroxide and its ultraviolet spectrum.[16]

The infrared spectrum of *trans*-α,β-diphenyl-*p*-methoxyacrylophenone contained a band in the carbonyl region at 6.05 μ. The ultraviolet spectrum exhibited maxima at 225 mμ (ε 20,000), and 294 mμ (ε 23,400).

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.08; H, 5.75. Found: C, 84.27; H, 5.75.

The infrared spectrum of *cis*-α,β-diphenyl-*p*-methoxyacrylophenone contained a band in the carbonyl region at 6.00 μ. The ultraviolet spectrum exhibited maxima at 220 mμ (ε 19,600) and 287.5 mμ (ε 35,000).

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73. Found: C, C, 84.49; H, 5.92.

trans-α,β-Diphenyl-p-methoxyacrylophenone oxide (II). Twenty-eight grams (0.089 mole) of *trans*-α,β-diphenyl-*p*-methoxyacrylophenone, m.p. 90–91° was suspended in 1 l. of methanol. To the mixture was added 180 ml. of 30% hydrogen peroxide in 180 ml. of 10% sodium hydroxide. The solution was stirred for approximately 8 hr. The time taken for the reaction to be completed varied with a slight variation in room temperature and therefore the reaction was allowed to continue until the melting point of the precipitate had risen to 130°. The precipitate was collected, washed with water, and dried. The crude yield was 29 g. After recrystallization from ethyl alcohol, the yield was 26 g. (88%) of product, m.p. 133.5–134.5°. In later preparations, this oxidation was carried out at 60–70° and the time taken for the reaction to be completed was about 30 min. The infrared spectrum of the compound contained a band at 6.0 μ. The ultraviolet spectrum exhibited maxima at 290–292 mμ (ε 21,900) and 219 mμ (ε 22,100).

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.30; H, 5.42.

β-(p-Anisyl-α-phenylacrylophenone oxide (III). Three grams (0.0095 mole) of β-(*p*-anisyl)-α-phenylacrylophenone prepared by the procedure of Das and Ghosh[17] was partially dissolved in 100 ml. of methanol and to this solution was added 9 ml. of 30% hydrogen peroxide and 9 ml. of 10% sodium hydroxide. The mixture was stirred at 60° for 1 hr. After cooling, the precipitated material was collected, washed with water, and recrystallized from methanol to give 1.5 g. (47.5%) of β-(*p*-anisyl)-α-phenylacrylophenone oxide, m.p. 133–134°. The infrared spectrum showed a band in the carbonyl region at 5.95 μ.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.13; H, 5.49.

Reaction of one equivalent of phenylmagnesium bromide with trans-α,β-diphenylacrylophenone oxide (I). To an ether solution of phenylmagnesium bromide prepared from 1.57 g. (0.01 mole) of bromobenzene and 0.24 g. (0.01 g.-atom) of magnesium was added 2.6 g. (0.009 mole) of I. After the epoxy ketone went into solution a white solid precipitated in the reaction flask. The mixture was stirred for 0.5 hr. before hydrolysis with a sulfuric acid ice mixture. Only starting material, identified by mixed melting point was obtained.

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[10] Microanalyses and active hydrogen determinations were done by Dr. G. Weiler and Dr. F. B. Strauss, Microanalytical Laboratory, 164 Banbury Road, Oxford, England. The infrared spectra were determined with Perkin-Elmer Model 21 spectrophotometer. Unless otherwise stated the melted film technique was used to prepare the sample. The ultraviolet spectra were determined in 95% ethanol with a recording spectrophotometer by Miss Olive Garty through the courtesy of Dr. Raymond Kurkjy of Bakelite Co., Bloomfield, N. J. The melting points were determined on a Fisher-Johns block.

[11] E. P. Kohler and E. M. Nygaard, *J. Am. Chem. Soc.*, **52**, 4128 (1930).

[12] It has recently been found by Dilgen and Enright that if the time of heating is limited to 5 min. a 90% yield of oxide can be consistently obtained.

[13] H. O. House, *J. Am. Chem. Soc.*, **76**, 1235 (1954).

[14] J. S. Buck and W. S. Ide, *J. Am. Chem. Soc.*, **54**, 3012 (1932).

[15] W. Dilthey and W. Schneider-Windmueller, *J. prakt. Chem.*, **159**, 273 (1942).

[16] W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **75**, 5990 (1953); **77**, 5134 (1955). H. H. Szmant and A. J. Basso, *J. Am. Chem. Soc.*, **74**, 4397 (1952).

[17] A. K. Das and B. N. Ghosh, *J. Chem. Soc.*, **115**, 817 (1919).

When the reaction mixture was refluxed for 7 hr. and then hydrolyzed, an ether- and water-insoluble solid settled out at the interface. This was removed by filtration and recrystallized from absolute ethanol to give 0.5 g. of 3(or 2)-bromo-2(or 3)-hydroxy-1,2,3-triphenyl-1-propanone (X), m.p. 196–198° dec. The ether solution contained more of this same compound and also some starting material. The estimated yield of X was 35%. The infrared spectrum of the compound contained bands at 2.94 μ and 5.98 μ characteristic of the hydroxyl and carbonyl groups, respectively.

Anal. Calcd. for $C_{21}H_{17}O_2Br$: C, 66.15; H, 4.46; Br, 21.0. Found: C, 65.6; H, 4.35; Br, 20.0.

Reaction of one equivalent of phenylmagnesium bromide with α,β-diphenyl-p-methoxyacrylophenone oxide (II). The procedure described above was repeated using 3.3 g. (0.01 mole) of II. One equivalent reacted at room temperature again yielded the unchanged oxide. When the reaction mixture was refluxed for 6 hr. before hydrolysis, an ether- and water-insoluble solid was obtained which was found to be a mixture of II and its bromohydrin 1-(*p*-anisyl)-3(or 2)-bromo-2(or 3)-hydroxy-2,3-diphenyl-1-propanone (XI). Recrystallization of the mixture from ethanol caused the bromohydrin to precipitate first. Both compounds were in the ethereal filtrate from which distinctly different crystalline forms separated. Recrystallization from absolute ethanol yielded 1.4 g. (34%) of XI m.p. 176–180° dec. The yield of recovered starting material was 0.7 g. The infrared spectrum of XI contained absorption bands at 2.90 μ and 5.98 μ characteristic of the hydroxyl and carbonyl groups, respectively.

Anal. Calcd. for $C_{22}H_{19}O_3Br$: C, 64.25; H, 4.62. Found: C, 64.04; H, 5.18.

Reaction of X *and* XI *with sodium methylate.* Two-tenths of a gram of X was placed in 25 ml. of 95% ethanol and to this mixture was added a solution prepared from 0.1 g. of sodium in 10 ml. of methanol. The mixture was allowed to stand at room temperature for 20 min. and then most of the solvent was removed under reduced pressure. A small amount of water was added and the precipitate which formed was filtered, washed with water, and dried to give a quantitative yield of I, m.p. 82°, identified by mixed melting point.

When the above procedure was carried out with XI, ring closure took place to yield II.

Reaction of trans-α,β-diphenylacrylophenone oxide (I) *with excess phenylmagnesium bromide at room temperature.* To an ether solution of phenylmagnesium bromide prepared from 0.97 g. (0.04 g.-atom) of magnesium and 6.28 g. (0.04 mole) of bromobenzene was added 2.8 g. (0.009 mole) of I. A slight amount of heat was evolved and the mixture was allowed to react at room temperature for 0.5 hr. and then hydrolyzed in a sulfuric acid–ice mixture. After the ether layer was washed successively with water, 10% sodium hydroxide, and water, it was dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. When the residual oil was taken up in methanol, a white solid, IV, precipitated, and evaporation of the filtrate gave more of the same compound. Recrystallization from methanol yielded white crystals, m.p., 132–133°. The total yield of 2,3-epoxy-1,1,2,3-tetraphenyl-1-propanol (IV) was 3.1 g. (87%). The infrared spectrum of IV contained an absorption band at 2.86 μ attributable to the hydroxyl group. There was no band in the carbonyl region of the spectrum. The residue from this reaction contained 0.32 g. of yellow oil, the infrared spectrum of which contained both carbonyl and hydroxyl absorption bands.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.68; H, 5.86. Found: C, 85.43; H, 5.73. Active Hydrogen: Calcd.: 0.264. Found: 0.25.

Reaction of trans-α,β-diphenyl-p-methoxyacrylophenone oxide (II) *with excess phenylmagnesium bromide at room temperature.* To an ether solution of phenylmagnesium bromide prepared from 1.94 g. (0.08 g.-atom) of magnesium and 8.4 ml. (0.08 mole) of bromobenzene was added with stirring 6.6 g. (0.02 mole) of I. After the solution was stirred at room temperature for 0.5 hr. it was worked up as in the above procedure and yielded 3.8 g. (49%) of 1-anisyl-2,3-epoxy-1,2,3-triphenyl-1-propanol, (Va) m.p. 145–146°.

Anal. Calcd. for $C_{28}H_{24}O_3$: C, 82.33; H, 5.92. Found: C, 81.98; H, 5.95. Active hydrogen. Calcd: 0.245. Found: 0.22.

Evaporation of the solvent gave 3.1 g. of yellow oil which was chromatographed on a column of reagent grade neutral alumina. The mixture was initially dissolved in petroleum ether b.p. (30–60°) to which sufficient benzene was added to keep the oil in solution. The column was eluted with the following series of solvents: petroleum ether (b.p. 30–60°), (50 ml.); petroleum ether–benzene (20 ml.:10 ml., 20 ml.:20 ml., 10 ml.:20 ml.); benzene (50 ml.); benzene-ether (30 ml.:10 ml., 20 ml.:20 ml., 10 ml.:30 ml.); ether (100 ml.); methanol (50 ml.). Biphenyl, m.p. 66–67°, was obtained from the petroleum ether fraction of the eluate.

Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.25; H, 6.55.

The ether fraction of the eluate gave a very small amount of solid, m.p. 64–65°, which after recrystallization from petroleum ether (b.p. 90–100°) did not depress the melting point of benzhydrol. Portions of oil which resisted crystallization were also obtained.

The benzene–ether portion of the eluate gave an oil which, when worked up in methanol, crystallized. Recrystallization from methanol gave a white solid m.p. 128–129°, which was identified as 1-anisyl-2,3-epoxy-1,2,3-triphenyl-1-propanol (Vb) the diastereomer of Va. This compound depressed the melting point of Va to 110–115° but did not depress the melting point of Vb obtained from the following procedure.

Reaction of trans-α,β-diphenylacrylophenone oxide (I) *with p-anisyl-magnesium bromide.* To a solution of *p*-anisylmagnesium bromide prepared from 0.97 g. (0.04 g.-atom) of magnesium and 7.48 g. (0.04 mole) of *p*-bromoanisole was added 2.8 g. (0.009 mole) of I. The gummy solid which settled out on the sides of the flask went into solution gradually as the solution was stirred at room temperature for 0.5 hr. When the reaction mixture was worked up in the usual manner two products were obtained, 0.4 g. (11%) of Va and 1.0 g. (27.3%) of Vb, identified by mixed melting points with these compounds obtained in the above reactions, and by a comparison of the infrared spectra. The mixed melting point of the two diastereomers shows a depression and although their infrared spectra are almost identical there is a slight difference in the relative height of two bands in the region of 800–825 cm.$^{-1}$, which is consistently observed in the spectra of the samples obtained from the various reactions.

Anal. (Vb) Calcd. for $C_{28}H_{24}O_3$: C, 82.33; H, 5.92. Found: C, 82.85; H, 6.11.

Reaction of β-(p-anisyl)-α-phenylacrylophenone oxide (III) *with excess phenylmagnesium bromide at room temperature.* To a solution of phenylmagnesium bromide, prepared from 0.97 g. (0.04 g.-atom) of magnesium and 4.2 ml. (0.04 mole) of bromobenzene in 60 ml. of absolute ether and diluted to 100 ml., was added 3.3 g. (0.01 mole) of III. The solution was stirred for 1 hr. and was then hydrolyzed with a 3% mixture. The ether layer was washed successively with sodium bicarbonate solution, sodium hydroxide solution, and water, then dried over anhydrous sodium sulfate. Evaporation of the ether under reduced pressure left a yellow solid which was recrystallized from methanol to give 3.4 g. (83%) of 3-anisyl-2,3-epoxy-1,1,2-triphenyl-1-propanol (VI), m.p. 130–134°. Two additional crystallizations from methanol raised the melting point to 138–139° and removed the color from the crystals. The infrared spectrum of this compound contained a hydroxyl band at 2.85 μ and no band in the carbonyl region.

Anal. Calcd. for $C_{28}H_{24}O_3$: C, 82.33; H, 5.92. Found: C, 82.80; H, 5.81.

Reaction of trans-α,β-diphenylacrylophenone oxide (I) *with excess phenylmagnesium bromide at reflux temperature.* To an ether solution of 5 equivalents of phenylmagnesium bromide prepared from 2.03 g. (0.08 g.-atom) of magnesium and 8.7 ml. (0.08 mole) of bromobenzene in 160 ml. of ether was added 5 g. (0.017 mole) of I. The mixture was refluxed for 21 hr. and then hydrolyzed with a cold saturated solution of ammonium chloride. The ether solution was extracted with a 5% solution of sodium hydroxide and then with a 15% solution of sodium bisulfite. No aldehyde was obtained from the bisulfite extract. The ether solution was dried over anhydrous sodium sulfate and the ether evaporated. When the residue was shaken with methanol the oil went into solution and three separate fractions of white crystals were obtained. The first and third fractions contained 3.9 g. (59%) of IV, m.p. 131–132°, which was identified by mixed melting point with the sample obtained when this reaction mixture was not refluxed, and by a comparison of the infrared spectra of the two samples. The second fraction contained 0.2 g. (4%) of solid, m.p. 110–120°, which was recrystallized from methanol to yield crystals, m.p. 135°. This substance did not depress the melting point of α-phenyldesoxybenzoin obtained from the acid cleavage of IV with hydrogen chloride, and the two samples had identical infrared spectra. The methanol filtrate was evaporated and the residual oil was chromatographed on an alumina column in a manner similar to that described above. Biphenyl, identified by mixed melting point with an authentic sample, was the first solid obtained from the chromatography. More α-phenyldesoxybenzoin and a small amount of benzhydrol, m.p. 66–67°, were obtained. The benzhydrol did not depress the melting point of an authentic sample and had an identical infrared spectrum.

The same products were obtained from this reaction when a 3% sulfuric acid–ice mixture was used to hydrolyze the reaction mixture.

Reaction of trans-α,β-diphenyl-p-methoxyacrylophenone oxide (II) *with excess phenylmagnesium bromide at reflux temperature.* To 215 ml. of an etheral solution of phenylmagnesium bromide prepared from 2.91 g. (0.12 g.-atom) of magnesium and 12.6 ml. (0.12 mole) of bromobenzene, was added 9.9 g. (0.03 mole) of *trans-α,β*-diphenyl-*p*-methoxyacrylophenone oxide (II). The reaction mixture was refluxed for 7 hr. and then allowed to stand overnight. After hydrolysis with an sulfuric acid–ice mixture, the ether layer was extracted with a 10% solution of sodium hydroxide and then with a 15% solution of sodium bisulfite. From the bisulfite extract benzaldehyde was obtained and identified by the mixed melting point of its 2,4-dinitrophenylhydrazone with that of an authentic sample. The ether solution was dried over anhydrous sodium sulfate and the solvent was removed. The residual oil weighed 15 g. and its infrared spectrum contained both carbonyl and hydroxyl bands. The oil was dissolved in petroleum ether (b.p. 30–60°) and benzene and was chromatographed on an alumina column in the manner previously described. The first fraction of the eluate evaporated to give a mixture of biphenyl, m.p. 66–67°, and a small amount of a white crystalline solid, m.p. 106–107°, which was separated from the biphenyl by fractional crystallization. The infrared spectrum of this compound showed neither hydroxyl nor carbonyl bands. On repeated runs of this reaction this product was not again isolated and its structure was not further investigated.

Anal. Found: C, 88.27; H, 6.14.

The second solid fraction obtained from the chromatography contained 4.1 g. of material which after recrystallization from methanol gave approximately 3 g. (25%) of Vb, identified by mixed melting point with this compound obtained from the same reaction at room temperature. The third solid fraction obtained from the chromatography weighed 2.1 g. and was recrystallized from petroleum ether (b.p. 90–100°) to give 1.5 g. of benzhydrol, m.p. 65–66°. The benzhydrol was identified by the comparison of its infrared spectrum with that of an authentic sample, by mixed melting point with the authentic sample, and by the preparation of the α-naphthylurethan, m.p. 136°, which did not depress the melting point of a known sample of this derivative. Portions of the eluate evaporated to give oils which resisted crystallization. When this reaction was repeated in an attempt to isolate other products, infrared analyses were done on various portions of the oils obtained, one of which was identical with that of a known sample of α-anisyldesoxybenzoin.

Cleavage and rearrangement of epoxyalcohols. To 15 ml. of glacial acetic acid, saturated with anhydrous hydrogen chloride, was added 0.8 g. (0.002 mole) of Vb and the solution was allowed to stand at room temperature for 2 hr. Most of the solvent was then removed under reduced pressure and to the residue was added a small amount of water and sodium bicarbonate. This mixture was shaken with a 15% solution of sodium bisulfite and then extracted with ether. Evaporation of the ether layer and recrystallization of the residue from methanol yielded 0.35 g. (0.012 mole, 58%) of α-anisyldesoxybenzoin, m.p. 89–90°. The infrared spectrum contained a band at 5.92 μ attributable to a conjugated carbonyl group. The compound was identified by the preparation of its oxime, m.p. 139–140° (lit.,[18] 139–140°).

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.50; H, 5.97. Found: C, 83.40; H, 6.28.

Sufficient sodium carbonate was added to the bisulfite layer to decompose the addition product and the solution was extracted with ether. Evaporation of the ether gave benzaldehyde which was identified by the preparation of its 2,4-dinitrophenylhydrazone, m.p. 237°. The melting point of a mixture with an authentic sample was not depressed.

The above procedure was repeated with Va and the same two products were obtained.

When the same procedure was carried out with 1 g. (0.0026 mole) of 2,3-epoxy-1,1,2,3-tetraphenyl-1-propanol (IV), 0.4 g. (0.0015 mole, 57%) of α-phenyldesoxybenzoin, m.p. 136–137° (lit.[13] m.p. 135–136°), was obtained, along with the benzaldehyde. The infrared spectrum of the ketone contained an absorption band at 5.95 μ attributable to a conjugated carbonyl group.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 87.60; H, 5.82.

A 50-mg. sample of VI was subjected to the same procedure. No aldehyde was isolated. Evaporation of the ether layer and treatment of the residue with methanol yielded *p*-methoxybenzyl phenyl ketone, m.p. 95°, which did not depress the melting point of an authentic sample prepared by the procedure of Buck and Ide.[14] The two samples had identical infrared spectra. Evaporation of the methanol filtrate yielded benzophenone identified by the preparation of its 2,4-dinitrophenylhydrazone, m.p. 230°, which did not depress the melting point of an authentic sample.

Reaction of trans-α,β-diphenylacrylophenone oxide (I) *with two equivalents of phenyllithium at room temperature.* To 57 ml. of an ethereal solution of phenyllithium containing approximately 0.02 mole of reagent in a nitrogen flushed apparatus was added 3 g. (0.01 mole) of I and the solution was stirred for 1 hr. The solution was hydrolyzed with a dilute sulfuric acid–ice mixture and the ether layer washed with a solution of sodium bicarbonate and then with a solution of sodium hydroxide. The bicarbonate washings did not yield any solid when acidified and extracted with ether. The ether layer was washed with distilled water and dried over anhydrous sodium sulfate. The residue from the evaporated ethereal solution when recrystallized from methanol yielded 3 g. (79.5%) of 2,3-epoxy-1,1,2,3-tetraphenyl-1-propanol (IV), m.p. 131–132°, identified by mixed melting point with this product from the reaction of I with phenylmagnesium bromide and by a comparison of infrared spectra.

Reaction of trans-α,β-diphenyl-p-methoxyacrylophenone oxide (II) *with two equivalents of phenyllithivm at room temperature.* To 80 ml. of an ethereal solution of phenyllithium

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(18) A. McKenzie and A. K. Mills, *Ber.*, **62**, 1784 (1929). A. Orekhoff and M. Tiffeneau, *Bull. soc. chim. France*, **29**, 445 (1921).

containing approximately 0.02 mole of reagent was added 3.3 g. (0.01 mole) of II while the apparatus was flushed with nitrogen. The mixture was stirred at room temperature for 2.5 hr. and was then worked up in the usual manner. No acid was obtained by extraction of the ether layer with bicarbonate. Evaporation of the dried ether solution left a viscous yellow oil which when dissolved in methanol yielded 2.4 g. (59%) of the 1-anisyl-2,3-epoxy-1,2,3-triphenyl-1-propanol (Vb), m.p. 127–128°. This product was identified by mixed melting point with the sample of the product obtained from the reaction of I with anisylmagnesium bromide and by a comparison of the infrared spectra of the two samples. Evaporation of the solvent left 1.3 g. of yellow oil from which other products were not obtained.

Reaction of trans-β-(p-anisyl)-α-phenylacrylophenone oxide (III) *with phenyllithium at room temperature.* To 70 ml. of an ethereal solution of phenyllithium containing approximately 0.013 mole of reagent was added 1.5 g. (0.0045 mole) of *trans*-β-(*p*-anisyl)-α-phenylacrylophenone oxide (III). The solution was allowed to react at room temperature for 1 hr. and then worked up in the usual manner. Evaporation of the dried ether solution gave an oil which when dissolved in methanol yielded 0.42 g. (41%) of *p*-methoxybenzyl phenyl ketone, m.p. 90°. Recrystallization from methanol raised the melting point to 95–96°. The product was identified by comparison with an authentic sample of *p*-methoxybenzyl phenyl ketone prepared by the procedure of Buck and Ide.[14] The mixed melting point was not depressed and the infrared spectra were identical.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.14; H, 5.94.

The residual oil from the methanol filtrate of this reaction mixture was extracted twice with petroleum ether (b.p. 30–60°). The second extract was evaporated and the residue dissolved in ethanol and treated with a solution of 2,4-dinitrophenylhydrazine to give a derivative which melted at 230° and did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of benzophenone.

Reaction of trans-α,β-diphenylacrylophenone oxide (I) *with four equivalents of phenyllithium at reflux temperature.* Three grams (0.01 mole) of *trans*-α,β-diphenylacrylophenone oxide (I) dissolved in 15 ml. of absolute ether was added to 84 ml. of a solution of phenyllithium containing approximately 0.04 mole of reagent, in a nitrogen flushed apparatus. During 3 hr. of refluxing the yellow solution turned from red to purple to black. After the usual work-up the residual oil left after the evaporation of the dried ether solution was shaken with methanol, and 0.2 g. of triphenylcarbinol, m.p. 160°, precipitated. This product was identified by mixed melting point with an authentic sample and by reduction to triphenylmethane, m.p. 92°.[19] The second fraction which precipitated from the methanol filtrate weighed approximately 1 g. and melted broadly at 90–130°. Two recrystallizations from methanol raised the melting point to 160–161°. This product depressed the melting point of triphenylcarbinol to 130° and its infrared spectrum contained a band in the carbonyl region at 6.0 μ and no band characteristic of the hydroxyl function.

Anal. Calcd. for $C_{33}H_{26}O$: O, 90.37; H, 5.97. Found: C, 90.45; H, 5.82.

The evaporation of the methanol filtrate left a viscous yellow oil which was chromatographed on an alumina column. Evaporation of the eluate yielded various portions of oils, one of which was dissolved in ethanol and treated with a solution of 2,4-dinitrophenylhydrazine to yield a derivative which, after recrystallization from methanol, melted at 198–200°, and did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of desoxybenzoin.

Reaction of trans-α,β-diphenyl-p-methoxyacrylophenone oxide (II) *with four equivalents of phenyllithium at reflux temperature.* To 60 ml. of an ethereal solution of phenyllithium containing 0.027 mole of reagent, was added 2.2 g. (0.0067 mole) of *trans*-α,β-diphenyl-*p*-methoxyacrylophenone oxide (II). The solution was refluxed for 3 hr. during which a bright orange color developed in the solution. After being worked up in the usual manner, the residue from the evaporation of the ether solution was dissolved in methanol and yielded 0.6 g. (22%) of 1-anisyl-2,3-epoxy-1,2,3-triphenyl-1-propanol (Vb) identified by mixed melting point and comparison of its infrared spectrum with samples of this compound obtained in previous reactions. Other products were not isolated from the residual oil which gave a positive test for the carbonyl function when treated with a solution of 2,4-dinitrophenylhydrazine.

Reaction of 2,3-epoxy-1,1,2,3-tetraphenyl-1-propanol (IV) *with four equivalents of phenyllithium at reflux temperature.* To 70 ml. of a solution of phenyllithium containing approximately 0.026 mole of reagent was added 2 g. (0.0067 mole) of 2,3-epoxy-1,1,2,3-tetraphenyl-1-propanol (IV). The solution was refluxed for 4 hr. during which the color darkened to a purplish black. The reaction mixture was worked up in the usual way. Solution of the residual oil from the ether evaporation in methanol yielded 0.5 g. of white crystals whose melting point after two recrystallizations from methanol was 160–161°. This compound did not depress the melting point of the unidentified carbonyl compound, $C_{33}H_{26}O$, obtained from the refluxing of I with phenyllithium and had an identical infrared spectrum. It did depress the melting point of triphenylcarbinol. The second fraction which precipitated gave, after further purification by recrystallization from methanol, both the carbonyl compound identified by mixed melting point and infrared spectrum, and triphenylcarbinol identified by mixed melting point and reduction to triphenylmethane.[20] The third fraction which precipitated, m.p. 45°, was treated with 2,4-dinitrophenylhydrazine and gave a derivative, which after recrystallization melted at 197–200° and did not depress the melting point of authentic sample of the 2,4-dinitrophenylhydrazone of desoxybenzoin.

Reaction of trans-α,β-diphenylacrylophenone oxide (I) *with one equivalent of phenyllithium at room temperature.* To 51 ml. of a solution of phenyllithium containing approximately 0.007 mole of reagent in a nitrogen flushed apparatus was added 1.9 g. (0.0063 mole) of I. The solution was allowed to react at room temperature for approximately 1 hr. and then worked up in the usual manner. The product was 1 g. of the starting epoxy ketone, identified by mixed melting point. No other products were isolated.

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(19) E. H. Huntress and S. P. Mulliken, "The Identification of Pure Organic Compounds," J. Wiley, New York, 1949, p. 423.