

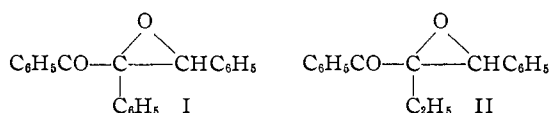
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Rearrangement of α,β -Epoxy Ketones. VII. The α -Ethylbenzalacetophenone Oxide SystemBY HERBERT O. HOUSE AND DONALD J. REIF¹

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The *cis* and *trans* isomers of α -ethylbenzalacetophenone oxide have been prepared. The isomerization of either isomer in the presence of boron trifluoride yielded 1,2-diphenyl-1,3-pentanedione.

An earlier study² of the acid-catalyzed rearrangement of the diastereoisomeric α -phenylbenzalacetophenone oxides (I) revealed that each diastereoisomer produced a different isomerization product. In order to learn whether the rearrangement of the other α -substituted α,β -epoxy ketones exhibits the stereospecificity observed with the oxides I, the diastereoisomeric α -ethylbenzalacetophenone oxides (II) have been prepared and their rearrangement has been studied.



The isomeric α -ethylbenzalacetophenones (III), required as precursors for the epoxides II, were prepared by the condensation of benzaldehyde with butyrophenone in the presence of hydrogen chloride followed by dehydrochlorination of the intermediate β -chloro ketone.^{3,4} After the proportion of the *cis*-isomer IIIb in the unsaturated ketone mixture III had been increased by irradiation with ultraviolet light, the isomeric ketones IIIa and IIIb were separated by fractional distillation. The configurations of the ketones III were established by relating them to α -ethyl-*trans*-cinnamic acid (IVa).⁵ The *cis*-acid IVb, previously obtained by irradiation of the *trans*-acid IV with ultraviolet light,⁶ also was prepared by carbonation of the organolithium compound⁷ derived from the bromide V; the bromide V was obtained by decarboxylative debromination⁸ of the *trans*-acid dibromide. The facile cyclization of only the *cis*-acid IVb to form the indenone VI⁶ established the configurations of the acids IV. Each of the isomeric acid chlorides VII was prepared by reaction of the sodium salt of the appropriate acid IV with oxalyl chloride. The *cis*-acid chloride VIIb could not be prepared by more conventional methods (*i.e.*, use of thionyl chloride or phosphorus pentachloride) because it was isomerized to the *trans*-acid chloride VIIa

under the conditions of the reaction. Each of the acid chlorides VII, characterized as their amides VIII, reacted with diphenylcadmium to produce the desired ketone III in poor yield. In one case the crude product from the *cis*-acid chloride VIIb was found to contain the indenone VI as well as the *cis*-ketone IIIb. The product from the *trans*-acid chloride VIIa was shown to contain both the expected *trans*-ketone IIIa and smaller amounts of the *cis*-ketone IIIb.

Reaction of the *trans*-unsaturated ketone IIIa with alkaline hydrogen peroxide produced the *trans*-epoxy ketone IIa. However, the *cis*-unsaturated ketone IIIb failed to react under these conditions. The failure of α -substituted-*cis*-benzalacetophenones to be epoxidized under these conditions would appear to be a general phenomenon, similar behavior having been observed previously with α -phenyl-*cis*-benzalacetophenone.^{2,9} Since the lack of reactivity of the *cis*-ketone IIIb might be attributed to the non-coplanarity (and consequent lack of conjugation) of the carbonyl group and the carbon-carbon double bond, we attempted to epoxidize the ketone IIIb with peracetic acid. However, only the unchanged ketone IIIb was isolated; none of the desired oxide IIb could be detected in the crude product. Consequently, the *cis*-epoxy ketone IIb was prepared by reduction of the unsaturated ketone with lithium aluminum hydride followed by epoxidation with peracetic acid and subsequent oxidation with chromium trioxide in pyridine.¹⁰

Since the isomerization of the epoxy ketones IIa and IIb occurred in very poor yield in the presence of boron trifluoride etherate, each isomerization was effected in the presence of a benzene solution of boron trifluoride gas. In each case the isomerization product was 1,2-diphenyl-1,3-pentanedione (IX) isolated either as the diketone IX or as the pyrazole X. There was no indication that either of the other probable rearrangement products XI or XII was present in any of the reaction mixtures.

The steric control observed² in the rearrangement of the α -phenylbenzalacetophenone oxides (I) involved cleavage of the epoxide ring in both possible directions XIII and XIV. At that time oxirane cleavage of the type XIII was regarded as anomalous since one of the resonance forms XVa contributing to this ion would be destabilized by

(9) These observations have led us to assign the configuration α -methyl-*trans*-benzalacetophenone oxide to the epoxide previously prepared (ref. 2) from α -methyl-*trans*-benzalacetophenone. Evidence pertaining to the stereochemistry of the unsaturated ketone has been presented by W. B. Black and R. E. Lutz, *THIS JOURNAL*, **77**, 5134 (1955).

(10) The epoxidation procedure was developed by H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955).

(1) Alfred P. Sloan Foundation Research Assistant.

(2) H. O. House and D. J. Reif, *THIS JOURNAL*, **77**, 6525 (1955).

(3) This procedure was employed by G. Albesco [*Ann. chim. (Paris)*, **9**], **18**, 221 (1922)] to prepare a sample of α -ethylbenzalacetophenone of unspecified stereochemical purity.

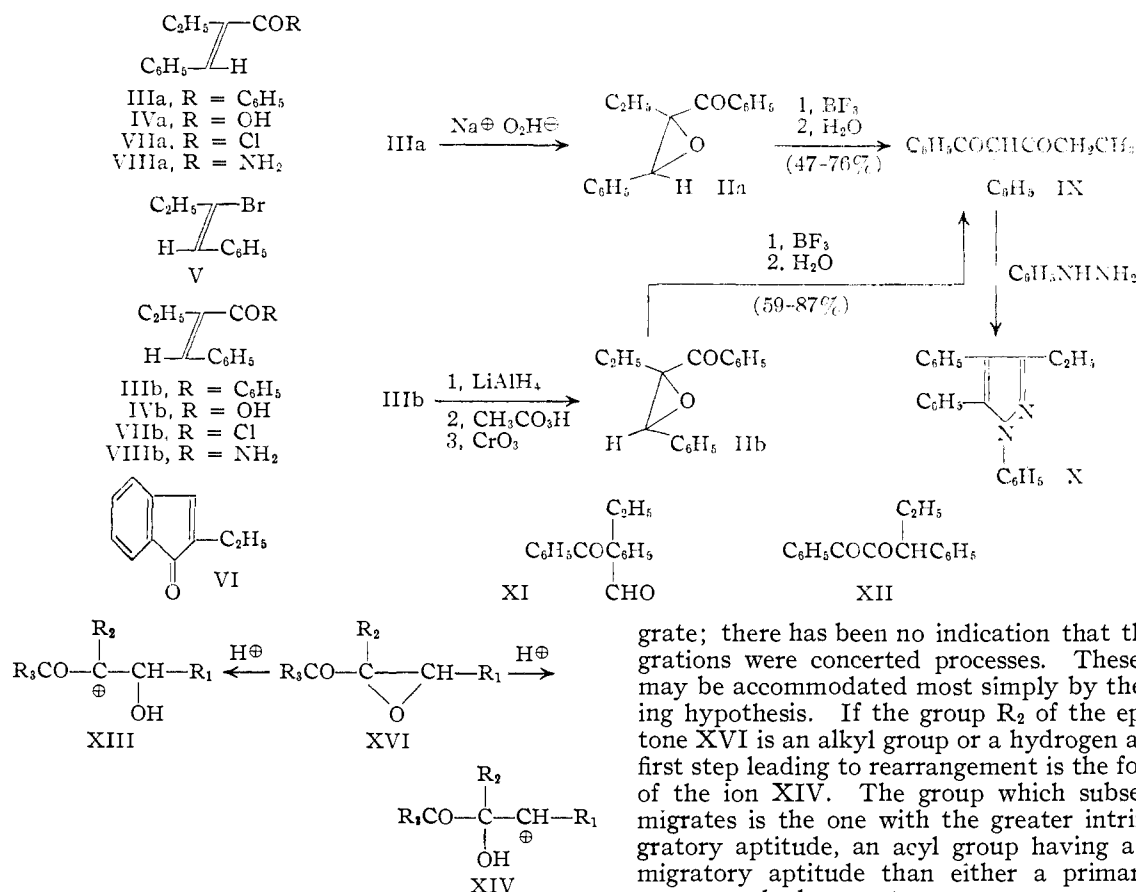
(4) This general method for the preparation of substituted benzalacetophenones was developed by E. P. Kohler [*Am. Chem. J.*, **31**, 642 (1904)].

(5) The *trans*-acid IVa was prepared by the method of W. H. Perkin [*J. Chem. Soc.*, **31**, 388 (1877)].

(6) R. Stoermer and G. Voht, *Ann.*, **409**, 47 (1915).

(7) The stereospecific formation of vinylolithium compounds has been reviewed by E. A. Braude in J. W. Cook, "Progress in Organic Chemistry," Vol. 3, Academic Press, Inc., New York, N. Y., 1955, pp. 191-99.

(8) The stereospecificity of the process has been established by E. Grovenstein, Jr., and co-workers, *THIS JOURNAL*, **75**, 2639 (1953); **77** 3795 (1955).



an unfavorable electrostatic interaction. However, subsequent experimental data¹¹ have indicated that a hydrogen atom and an acyl group affect the stability of an adjacent carbonium ion to about the same degree. An explanation for this result may lie in the additional resonance stabilization gained from XVc which could offset the energy lost from the greatly diminished contribution form XVa.

Thus, the type of steric control observed in the rearrangement of the keto oxides I would be expected only when the groups R₁ and R₂ of the keto oxide XVI can stabilize the possible incipient carbonium ions XIII and XIV to approximately the same extent. The fact that each of the diastereoisomeric oxides I yielded a different rearrangement product indicates that the cleavage of the oxide ring and the migration of a phenyl group were concerted processes.² In other cases,¹² including the present report, where the rearrangement of diastereoisomeric pairs of α,β-epoxy ketone XVI has been investigated the nature of the groups R₂ (= H or alkyl) and R₁ (= phenyl) has favored the formation of the intermediate ion XIV. In these cases the acyl group always has been found to mi-

(11) H. O. House, D. J. Reif and R. L. Wasson, *THIS JOURNAL*, **79**, 2490 (1957).

(12) H. O. House, *ibid.*, **76**, 1235 (1954).

grate; there has been no indication that these migrations were concerted processes. These results may be accommodated most simply by the following hypothesis. If the group R₂ of the epoxy ketone XVI leading to rearrangement is the formation of the ion XIV. The group which subsequently migrates is the one with the greater intrinsic migratory aptitude, an acyl group having a greater migratory aptitude than either a primary alkyl group or a hydrogen atom.

Experimental¹³

α-Ethyl-*cis*-cinnamic Acid (IVb) and Derivatives.—A solution of 1.5 g. (0.0071 mole) of 2-bromo-*trans*-1-phenyl-1-butene¹⁴ in 15 ml. of ether was added, dropwise and with stirring over a period of 1 hr., to a suspension of 0.13 g. (0.018 gram-atom) of lithium wire in 25 ml. of ether. The resulting mixture was stirred for 4 hr. The reaction temperature was maintained at -20 to -28° throughout the reaction. The resulting mixture was poured into a slurry of Dry Ice in ether, allowed to stand overnight, then washed with dilute, aqueous acid and, finally, extracted with aqueous sodium bicarbonate. After the bicarbonate extract had been acidified and extracted with ether, the ether solution was dried over magnesium sulfate and concentrated. A solution of the residual oil in benzene, when treated with excess aniline and cooled, deposited the aniline salt of α-ethyl-*cis*-cinnamic acid which separated as white needles, m.p. 80.6–81.2° (lit.⁶ 81°), yield 0.55 g. (29%). No α-ethyl-*trans*-cinnamic acid could be isolated from the mother liquor. The non-acidic fraction from the reaction mixture (320 mg. of oil) was examined by vapor-phase chromatography¹⁵; in addition to 10% of the unchanged 2-bromo-*trans*-

(13) All melting points are corrected and all boiling points are uncorrected. The ultraviolet spectra were determined in 95% ethanol with a Cary recording spectrophotometer, model 11 MS. The infrared spectra were determined either with a Baird, model B, or a Perkin-Elmer, model 21, double beam infrared recording spectrophotometer fitted with a sodium chloride prism. The microanalyses were performed by Dr. S. M. Nagy and his associates.

(14) A sample of 2-bromo-1-phenyl-1-butene, b.p. 126–128° (23 mm.), of unspecified stereochemistry was previously prepared by M. T. Bogert and D. Davidson, *THIS JOURNAL*, **54**, 334 (1932). Our sample, b.p. 126.5–127.5° (20 mm.), *n*_D²⁰ 1.5756, λ_{max} 251 mμ (ε 12,700), was shown to be 92.3% stereochemically pure by vapor-phase chromatography (ref. 15).

(15) The apparatus consisted of a 8 mm. × 215 cm. column packed with Dow Silicone Oil No. 550 suspended on 50–80 mesh ground firebrick. The samples eluted with helium were detected with a thermal conductivity cell.

1-phenyl-1-butene at least four other components were present.

An attempt to exchange the bromoolefin with butyllithium in a benzene-ether mixture followed by carbonation resulted in the recovery of 77% of the bromoolefin. No non-volatile acid could be isolated.

A solution of the aniline salt of α -ethyl-*cis*-cinnamic acid in ether was washed with dilute aqueous acid, dried over magnesium sulfate and concentrated. When a solution of the residue in petroleum ether was cooled, α -ethyl-*cis*-cinnamic acid separated as white needles, m.p. 36.8–37.8°. The infrared spectrum¹⁶ of the acid has a broad band with its center at 2980 cm^{-1} as well as a band at 1695 cm^{-1} . The ultraviolet spectrum has a maximum at 253.5 $\text{m}\mu$ (ϵ 12,300).

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}$: C, 74.97; H, 6.86. Found: C, 74.66; H, 6.96.

The product was shown to be identical with the acid obtained by irradiation of α -ethyl-*trans*-cinnamic acid with ultraviolet light⁶ both by a mixed melting point determination and by comparison of the spectra of the two samples.

In order to prepare the amide, a suspension of 0.5 g. (0.0025 mole) of sodium α -ethyl-*cis*-cinnamate in 10 ml. of benzene containing three drops of pyridine was cooled in an ice-bath and treated with 0.3 ml. (0.45 g., 0.0035 mole) of oxalyl chloride. After the mixture had been allowed to stand for 5 min. in an ice-bath and an additional 15 min. at room temperature, the crude acid chloride was treated with excess aqueous ammonium hydroxide and then worked up in the usual manner. Pure α -ethyl-*cis*-cinnamamide crystallized from a benzene-petroleum ether mixture as white needles, m.p. 108.8–109.8°, yield 147 mg. (33%).

The infrared spectrum¹⁶ of the amide contains absorption bands at 3425 and 3325 cm^{-1} and at 1655 and 1640 cm^{-1} . The ultraviolet spectrum has a maximum at 253 $\text{m}\mu$ (ϵ 13,400).

Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{NO}$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.28; H, 7.60; N, 7.99.

Attempts to prepare the *cis*-acid chloride VIIb by reaction of the *cis*-acid with either thionyl chloride or phosphorus pentachloride resulted in isomerization. Treatment of these reaction mixtures with ammonium hydroxide produced the *trans*-amide VIIa accompanied in some cases by the *trans*-acid IVa. Similar results were obtained when the product from the reaction of sodium α -ethyl-*trans*-cinnamate and oxalyl chloride was heated.

α -Ethyl-*trans*-benzalacetophenone (IIIa).—A solution of 19.8 g. (0.102 mole) of α -ethyl-*trans*-cinnamoyl chloride, b.p. 98–101° (1.2 mm.) (lit.⁵ 142° (14 mm.)) [prepared from the *trans*-acid, m.p. 105–106° (lit.⁵ 104°), λ_{max} 266 $\text{m}\mu$ (ϵ 17,400), and thionyl chloride and characterized as the *trans*-amide VIIa, m.p. 132.2–133.2° (lit.⁵ 128°), λ_{max} 259 $\text{m}\mu$ (ϵ 14,700)] in 60 ml. of benzene was added, dropwise and with stirring over a period of 15 min. under an atmosphere of nitrogen, to a cold suspension of diphenylcadmium¹⁷ in benzene, prepared from 13.2 g. (0.075 mole) of anhydrous cadmium chloride and 70 ml. of an ether solution which contained 0.15 mole of phenylmagnesium bromide. After the addition was complete the mixture was boiled under reflux, with stirring, for 3 hr. After the biphenyl had been removed from the reaction mixture by steam distillation, an ether solution of the non-volatile material was washed with a saturated aqueous solution of sodium carbonate and then with water, dried over magnesium sulfate and the ether was removed. The residual crude oil was distilled under reduced pressure, the product being collected in three fractions, total weight 16.51 g., b.p. range 144–158° (0.4 mm.), n_{D}^{20} 1.6000–1.6054. The product, analyzed by vapor-phase chromatography, was composed of α -ethyl-*trans*-benzalacetophenone and α -ethyl-*cis*-benzalacetophenone in an approximate ratio of 3:1. The pure liquid α -ethyl-*trans*-benzalacetophenone, separated from the mixture by vapor-phase chromatography, boiled at 128–130° (0.35 mm.), n_{D}^{20} 1.6070. The α -ethyl-*trans*-benzalacetophenone was crystallized from a methanol-water mixture and followed by recrystallization from hexane. The pure *trans*-ketone separated as white needles, m.p. 47.5–48.5°, yield 2.53 g. (9.5%). The infrared spectrum¹⁸ contains absorption bands at 1650

and 1620 cm^{-1} . There is also a band at 1246 cm^{-1} which is not present in the spectrum of the *cis* isomer. The ultraviolet spectrum has maxima at 221 $\text{m}\mu$ (ϵ 10,700), 257 $\text{m}\mu$ (ϵ 12,100) and 289 $\text{m}\mu$ (ϵ 15,300).

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}$: C, 86.40; H, 6.83. Found: C, 86.61; H, 7.07.

The α -ethyl-*cis*-benzalacetophenone, isolated from the ketone mixture by vapor-phase chromatography, was distilled under reduced pressure. The α -ethyl-*cis*-benzalacetophenone, collected as a yellow oil, b.p. 128–130° (0.38 mm.), n_{D}^{20} 1.5964, amounted to 2.1 g. (7.9%). The infrared and ultraviolet spectra of this product were identical with the spectra of an authentic sample of the *cis*-ketone prepared as subsequently described.

In a second experiment the *trans*-acid chloride, prepared from sodium α -ethyl-*trans*-cinnamate and oxalyl chloride at room temperature and used without distillation, was treated with diphenylcadmium as previously described. The products isolated were the unchanged *trans*-acid (42% recovery) and a mixture of unsaturated ketones (2.6% yield) composed of 53.5% α -ethyl-*trans*-benzalacetophenone and 46.5% of α -ethyl-*cis*-benzalacetophenone.

α -Ethyl-*cis*-benzalacetophenone (IIIb).—A benzene solution of the *cis*-acid chloride, prepared from 12.08 g. (0.061 mole) of sodium α -ethyl-*cis*-cinnamate, and 6.0 ml. (0.07 mole) of oxalyl chloride as previously described, was added dropwise and with stirring over a period of 30 min. to a cold suspension of diphenylcadmium,¹⁷ prepared from 7.33 g. (0.04 mole) of anhydrous cadmium chloride and 0.088 mole of phenylmagnesium bromide, in benzene. After the addition was complete, stirring was continued for 4 hr. at 25–30°. An ether solution of the crude reaction product was allowed to stand, with occasional shaking, in contact with a saturated aqueous solution of sodium bicarbonate for one week to effect complete hydrolysis of any unchanged acid chloride present. The unchanged α -ethyl-*cis*-cinnamic acid was isolated as its aniline salt, recovery 1.15 g. (10.7%), and identified by a mixed melting point determination.

A hexane solution of the neutral fraction from the reaction mixture was chromatographed on Merck acid-washed alumina. The first 6 fractions contained crude biphenyl. The next 8 fractions containing the crude ketone, were eluted with hexane, combined and distilled. Pure α -ethyl-*cis*-benzalacetophenone was collected as a yellow oil, b.p. 128–130° (0.38 mm.), n_{D}^{20} 1.5963, yield 2.31 g. (16%). The product, analyzed by vapor-phase chromatography, contained only the *cis* isomer. The pure liquid ketone crystallized as white needles, m.p. 32–33°, from a methanol-water mixture.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}$: C, 86.40; H, 6.83. Found: C, 86.27; H, 6.67.

The infrared spectrum¹⁸ of the ketone contains an absorption band at 1657 cm^{-1} . There is also a band at 1230 cm^{-1} which is not present in the spectrum of the *trans* isomer. The ultraviolet spectrum has a maximum at 247 $\text{m}\mu$ (ϵ 22,100) with a point of inflection at 287 $\text{m}\mu$ (ϵ 4,250).

A second experiment was carried out as previously described except that the reaction time for the preparation of the acid chloride was extended to 1.5 hr. and the reaction time with diphenylcadmium was increased to 8 hr. Examination of the crude mixture by vapor-phase chromatography indicated a complex mixture containing only a small amount of the desired *cis*-ketone. The neutral products isolated from the reaction mixture were crude biphenyl and crude 2-ethylidenone, a bright yellow oil, collected at 140–150° (10 mm.), yield 12%. The infrared spectrum¹⁸ of the ketone contains an absorption band at 1710 cm^{-1} (conj. C=O in a five-membered ring). The ultraviolet spectrum has maxima at 236 $\text{m}\mu$ (ϵ 21,800) and 242 $\text{m}\mu$ (ϵ 25,300). A sample of the crude ketone (250 mg.) was treated with 2,4-dinitrophenylhydrazine in the usual manner. The 2,4-dinitrophenylhydrazone of 2-ethylidenone separated as tiny crystals melting with decomposition at 247–248°, yield 280 mg. (49%).

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_4$: C, 60.35; H, 4.17; N, 16.56. Found: C, 60.29; H, 4.19; N, 16.53.

The acidic products isolated from the reaction mixture were α -ethyl-*trans*-cinnamic acid, yield 8.1%, and α -ethyl-*cis*-cinnamic acid as its aniline salt, yield 10%. Mixed melting point determinations with authentic samples identified both products.

(16) Determined in chloroform solution.

(17) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., p. 324.

(18) Determined in carbon tetrachloride solution.

Aldol Condensation of Butyrophenone and Benzaldehyde.³

The product obtained by the condensation of benzaldehyde with butyrophenone followed by dehydrochlorination of the crude chloro ketone with quinoline was shown by vapor-phase chromatographic analysis¹⁵ to contain 70% of the *trans*-ketone and 30% of the *cis*-ketone. The mixture was dissolved in 100 ml. of hexane and irradiated with ultraviolet light (mercury-vapor arc) for 24 hr. Vapor-phase chromatographic analysis¹⁵ of the resulting mixture indicated the composition of the mixture was 50% *trans*-ketone and 50% *cis*-ketone. The ketone mixture was separated by repeated fractional distillation through a spinning band column. The yield of the α -ethyl-*cis*-benzalacetophenone, b.p. 115° (0.25 mm.), n_D^{25} 1.5965, was 22.6%. The yield of α -ethyl-*trans*-benzalacetophenone, m.p. 47.5–48.5°, was 30.8%.

α -Ethyl-*trans*-benzalacetophenone Oxide (IIa).—To a solution of 5 g. (0.0212 mole) of α -ethyl-*trans*-benzalacetophenone in 80 ml. of methanol was added 6.0 ml. (0.0624 mole) of a 30% aqueous solution of hydrogen peroxide and the mixture was cooled to 8°. Two milliliters (0.012 mole) of 6 *N* aqueous sodium hydroxide was added dropwise and with stirring. After the addition was complete, the cooling-bath was removed and stirring was continued for 36 hr.; the reaction was followed by the change in the optical density of the reaction mixture at 289 μ . Additional 6.0-ml. quantities of hydrogen peroxide were added after 2, 15, 19 and 26 hr. The reaction mixture was poured into water and the resultant mixture was extracted with two portions of ether. The combined organic layers were dried over magnesium sulfate and the solvents removed. Pure α -ethyl-*trans*-benzalacetophenone oxide crystallized from a methanol-water mixture as white needles, m.p. 37.0–38.0°, yield 3.2 g. (60%). The infrared spectrum¹⁶ of the oxide contains an absorption band at 1680 cm^{-1} . The ultraviolet spectrum has a maximum at 248 μ (ϵ 15,200).

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_2$: C, 80.92; H, 6.39. Found: C, 81.14; H, 6.45.

Rearrangement of α -Ethyl-*trans*-benzalacetophenone Oxide (IIa).—A solution of 1.0 g. (0.00394 mole) of the oxide in 30 ml. of dry benzene was saturated with boron trifluoride gas and allowed to stand at room temperature for 30 min. The mixture was then diluted with ether and washed with water. The solvents were removed and the crude solid which remained was recrystallized from ethanol. After an additional recrystallization from methanol followed by two recrystallizations from petroleum ether the pure keto form of 1,2-diphenyl-1,3-pentanedione separated as white needles, m.p. 93.0–95.0°, yield 464 mg. (47%).

The infrared spectrum¹⁶ of the diketone contains absorption bands at 1712 and 1675 cm^{-1} . The ultraviolet spectrum has an absorption peak at 247 μ (ϵ 11,300) and a broad plateau whose center is at 305 μ (ϵ 2,500). The latter peak may well be the result of partial enolization when the diketone was dissolved in ethanol.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_2$: C, 80.92; H, 6.39. Found: C, 80.65; H, 6.65.

When an alcoholic solution of 101 mg. (0.00039 mole) of the diketone was treated with 60 mg. (0.00056 mole) of phenylhydrazine and 0.4 ml. (0.007 mole) of acetic acid, as described subsequently, 110 mg. (85%) of 3-ethyl-1,4,5-triphenylpyrazole, m.p. 138.0–139.0°, was obtained. A mixed melting-point determination with the pyrazole subsequently prepared showed no depression.

In another experiment 254 mg. (0.001 mole) of the oxide was isomerized as previously described. A solution of the crude rearrangement product in ethanol was treated with 166 mg. (0.0015 mole) of phenylhydrazine and 0.4 ml. (0.007 mole) of acetic acid and boiled under reflux for 1 hr. The hot solution was filtered, diluted with water and cooled. The crude solid, collected on a filter, was recrystallized from hexane. The pure 3-ethyl-1,4,5-triphenylpyrazole crystallized as white needles, m.p. 138.0–139.0°, yield 245 mg. (76%). The ultraviolet spectrum of the pyrazole exhibits a maximum at 261 μ (ϵ 16,000) and a point of inflection at 227 μ (ϵ 20,200).¹⁹

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{N}_2$: C, 85.15; H, 6.21; N, 8.64. Found: C, 84.92; H, 6.40; N, 8.60.

(19) The corresponding values for 3-methyl-1,4,5-triphenylpyrazole (ref. 2) are 265 μ (ϵ 15,700) and 233 μ (ϵ 21,200).

Three additional isomerizations were carried out as described above with reaction times of 10 min., 1 hr. and 2 hr. The yields of pyrazole were 68.5, 66.5 and 60%, respectively. In an effort to isolate any 1,3-diphenyl-1,2-pentanedione (XII) present as its quinoxaline the crude rearrangement product was boiled with a solution of *o*-phenylenediamine dihydrochloride in ethanol. No quinoxaline derivative could be isolated. As a control experiment the α -ethyl-*trans*-benzalacetophenone oxide was treated with a boiling alcoholic solution of phenylhydrazine as described above. No pyrazole could be isolated.

Cleavage of 1,2-Diphenyl-1,3-pentanedione (XV) with Alcoholic Potassium Hydroxide.—A solution of the diketone (120 mg., 0.00047 mole) in 20 ml. of alcohol was treated with 30 mg. (0.00054 mole) of potassium hydroxide and boiled under reflux for 1 hr. The mixture was then poured into water and the neutral organic material was removed by extraction with ether. The solvents were removed from the extract and a solution of the residue in alcohol was treated with 100 mg. (0.0005 mole) of 2,4-dinitrophenylhydrazine in the usual manner. The resulting mixture was filtered while hot to leave 62 mg. (35%) of desoxybenzoin 2,4-dinitrophenylhydrazone, m.p. 201–203°, on the filter. A mixed melting point determination with an authentic sample showed no depression. Concentration of the mother liquor afforded 62 mg. of a mixture of 2,4-dinitrophenylhydrazones which melted at 115–125°. The mixture could not be separated either by fractional crystallization or by chromatography on alumina. The 2,4-dinitrophenylhydrazone of 1-phenyl-2-butanone, the other product expected from the cleavage, is reported to melt at 145.8–146.8°. ²⁰

Concentration of the alkaline extract from the original reaction mixture followed by acidification with hydrochloric acid afforded 20 mg. (35%) of benzoic acid, m.p. 121–122°. A mixed melting point determination with an authentic sample showed no depression.

Attempted Epoxidation of α -Ethyl-*cis*-benzalacetophenone (IIIB).—The behavior of a mixture of α -ethyl-*cis*-benzalacetophenone, hydrogen peroxide, methanol and sodium hydroxide was followed by measuring the optical density of the reaction mixture at 287 μ . After 48 hr. the reaction was stopped since the optical density of the reaction mixture indicated that no reaction had occurred. The recovered α -ethyl-*cis*-benzalacetophenone, identified by its infrared spectrum, amounted to 61.4%. Similarly, when a mixture of α -ethyl-*cis*-benzalacetophenone, a solution of peracetic acid in acetic acid, sodium acetate trihydrate and methylene chloride was stirred for 30 hr. and then worked up in the usual manner, only the unchanged *cis*-ketone (31.2% recovery) was isolated. The solvent was removed from the mother liquor to leave 150 mg. (37.5% recovery) of an oil whose infrared spectrum¹⁶ was very similar to the spectrum of the starting ketone and contained no bands which indicated the presence of α -ethyl-*cis*-benzalacetophenone oxide.

2-Ethyl-*cis*-1,3-diphenyl-2-propen-1-ol.—A mixture of 1.6 g. (0.0423 mole) of lithium aluminum hydride, 10.0 g. (0.0423 mole) of α -ethyl-*cis*-benzalacetophenone and 75 ml. of ether was stirred for 14 hr. at room temperature and then worked up as previously described.²¹ The crude product, an oil, was distilled in a short-path still under reduced pressure. The 2-ethyl-*cis*-1,3-diphenyl-2-propen-1-ol, collected at approximately 150° (0.20 mm.), amounted to 7.5 g. (73.5%). The infrared spectrum¹⁶ contains absorption bands at 3620 and 3470 cm^{-1} . The ultraviolet spectrum has a maximum at 243 μ (ϵ 13,800).

Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}$: C, 85.67; H, 7.61. Found: C, 85.21; H, 7.60.

The analytical results indicate that the alcohol is impure; however, an attempt to purify the sample by chromatography over Merck acid-washed alumina followed by distillation resulted in decomposition of the sample.

2-Ethyl-*cis*-2,3-epoxy-1,3-diphenyl-1-propanol.—A mixture of 6.0 g. (0.0252 mole) of crude 2-ethyl-*cis*-1,3-diphenyl-2-propen-1-ol, in 75 ml. of methylene dichloride, and 5 ml. of a solution containing 0.0326 mole of peracetic acid in acetic acid, in which 1.0 g. of sodium acetate trihydrate had been dissolved, was stirred for 30 min. at 5° and then at room temperature for 17 hr. The reaction was followed by the change in the optical density of the reaction mixture at 243

(20) M. S. Newman and A. Kutner, *This Journal*, **73**, 4199 (1951).

(21) H. O. House, *ibid.*, **78**, 2298 (1956).

m μ . The reaction mixture was worked up as previously described,²¹ the crude product being recrystallized from hexane. The pure 2-ethyl-*cis*-2,3-epoxy-1,3-diphenyl-1-propanol separated as white needles, m.p. 98.8–99.8°, yield 4.56 g. (71.2%). The infrared spectrum¹⁶ of the epoxy alcohol contains absorption bands at 3630 and 3520 cm.⁻¹. The ultraviolet spectrum had a maximum at 260 m μ (ϵ 46).

Anal. Calcd. for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.10; H, 7.12.

α -Ethyl-*cis*-benzalacetophenone Oxide (Iib).—A solution of 4.0 g. (0.0158 mole) of 2-ethyl-*cis*-2,3-epoxy-1,3-diphenyl-1-propanol in 30 ml. of pyridine was oxidized with the chromium trioxide–pyridine complex,²² prepared from 100 ml. of pyridine and 10 g. (0.10 mole) of chromium trioxide, as described by Wasserman and Aubrey.¹⁰ The pure α -ethyl-*cis*-benzalacetophenone oxide crystallized from hexane as white needles melting at 81.5–82.5°, yield 2.90 g. (73%). The infrared spectrum¹⁶ contains an absorption band at 1688 cm.⁻¹ and has no band in the 3 μ region attributable to a hydroxyl group. The ultraviolet spectrum has an absorption peak at 250 m μ (ϵ 12,300).

Anal. Calcd. for C₁₇H₁₆O₂: C, 80.92; H, 6.39. Found: C, 80.95; H, 6.66.

Rearrangement of α -Ethyl-*cis*-benzalacetophenone Oxide (Iib).—A solution of 254 mg. (0.001 mole) of the oxide in 12 ml. of benzene was saturated with boron trifluoride gas and allowed to stand at room temperature for 2 hr. After the mixture had been diluted with ether and washed with water, the solvents were removed and the crude solid which remained was recrystallized from alcohol. An additional recrystallization from methanol followed by two recrystallizations from petroleum ether afforded the pure keto form of 1,2-diphenyl-1,3-pentanedione, m.p. 93.0–95.0°, as white needles, yield 150 mg. (59%). A mixed melting point determination with the diketone obtained from the *trans*-oxide showed no depression.

In another experiment 254 mg. (0.001 mole) of the oxide was isomerized as previously described. A solution of the crude rearrangement product in alcohol was treated with 166 mg. (0.0015 mole) of phenylhydrazine and 0.4 ml. (0.007 mole) of acetic acid as previously described. The yield of 3-ethyl-1,4,5-triphenylpyrazole, m.p. 138.0–139.0°, was 282 mg. (87%). A mixed melting point determination with the pyrazole sample previously described showed no depression. When the reaction time for the rearrangement was 30 min. the yield of the pyrazole was 282 mg. (87%).

As a control experiment the α -ethyl-*cis*-benzalacetophenone oxide (254 mg., 0.001 mole) was treated with phenyl-

(22) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *THIS JOURNAL*, **75**, 422 (1953).

hydrazine under the conditions used to prepare the derivative. The only material which could be isolated was the starting oxide, m.p. 81.0–82.0°, recovery 93%.

The infrared spectra¹⁶ of the crude reaction products obtained from the isomerizations of α -ethyl-*cis*-benzalacetophenone oxide and α -ethyl-*trans*-benzalacetophenone oxide were compared. The main constituent of each reaction mixture appeared to be the borofluoride complex of an enolized β -dicarbonyl compound (strong, relatively sharp band at 1555 cm.⁻¹).²³ Since neither of the spectra exhibit absorption in the 2700–2800 cm.⁻¹ region we regard the presence of any significant quantity of α -formyl- α -phenylbutyrophenone (XI), a possible rearrangement product, as very improbable.²⁴ The spectra of the two crude products differ only in the intensities of three weak bands found at 1675, 1710 and 1742 cm.⁻¹, these bands being more intense in the spectrum of the crude rearrangement product obtained from α -ethyl-*trans*-benzalacetophenone oxide. The bands of approximately equal intensity at 1675 and 1710 cm.⁻¹ are judged to represent a small amount of 1,2-diphenyl-1,3-pentanedione, the product isolated from each rearrangement after complete hydrolysis of the borofluoride complex. To verify this hypothesis the crude rearrangement product from the *trans*-oxide was recrystallized from methanol; the resultant solid after successive recrystallizations from methanol and hexane afforded pure 1,2-diphenyl-1,3-pentanedione, m.p. 92.5–94.5°, yield 47%. The infrared spectrum¹⁶ of the residue from the combined mother liquors exhibits the bands at 1675 and 1710 cm.⁻¹ as well as a broad band with its center at 1600 cm.⁻¹ (enolized β -dicarbonyl compound). The relative intensity of the band at 1742 cm.⁻¹ increased indicating that the component represented by this band has been concentrated by the partial removal of the 1,2-diphenyl-1,3-pentanedione. However, we were unable to isolate the small amount of this second component present in the reaction mixture. The location of band 1742 cm.⁻¹ attributed to this second component suggests that the material is not either of the two expected rearrangement products, α -formyl- α -phenylbutyrophenone (XI) or 1,3-diphenyl-3-ethyl-1,2-propanedione (XII).²⁵

(23) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 126.

(24) Absorption in this region, attributable to the C–H stretching vibration of an aldehyde function, is clearly discernible in the spectra of analogous compounds (see ref. 12).

(25) The absorption peaks attributable to the carbonyl functions in the homologous compounds, α -formyl- α -phenylpropiofenone and 1,3-diphenyl-1,2-propanedione, are found at 1670 and 1730 cm.⁻¹ and 1630 and 1705 cm.⁻¹, respectively.

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[CONTRIBUTION FROM THE MEMORIAL UNIVERSITY OF NEWFOUNDLAND]

Electronic Spectra and Molecular Dimensions. II.^{1,2} The "Buttrussing Effect" and Other Secondary Steric Interactions in Electronic Spectra

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Steric interactions are known to directly affect the main band (B-band) in ultraviolet absorption spectra. Developing the concept of steric hindrance, the so-called buttrussing effect is examined, and it is shown that some other changes affecting both wave length shifts and absorption intensities can be rationalized by assuming the operation of more extended or indirect steric interactions.

Introduction

Steric effects in the B-band of ultraviolet absorption spectra have been shown³ to give rise to various changes. If the steric inhibition of reso-

nance is large and the coplanarity of the molecule is almost completely destroyed, bands occur which may be regarded as partial chromophore bands, that is, the molecule absorbs as two or more distinct entities.⁴ If the steric interaction is less pronounced in comparison with a planar reference molecule, a wave length shift (usually to shorter wave length) accompanied by decreased absorption

(1) Presented before the Division of Organic Chemistry at the Miami Meeting of the American Chemical Society, April, 1957.

(2) Part I, *Can. J. Chem.*, **34**, 1542 (1956).

(3) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955); W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **34**, 1340, 1347 (1956); **35**, 488 (1957).

(4) Cf. L. W. Pickett, *et al.*, *THIS JOURNAL*, **72**, 44 (1950); **58**, 2296 (1936); E. Mueller and H. Neuhoß, *Ber.*, **72**, 2063 (1939).