butene-1-ol resulting from S_N2'[26] attack of azide ion on the oxide. 4-Azido-2-butene-1-ol might also, although less probably, have arisen through an allylic rearrangement of either 1-azido-2-butene-2-ol or 2-azido-3-butene-1-ol.

Most of the azidoalcohols studied were at least moderately stable. However, 1,3-diazido-2-propanol, which was the only product isolated from the reaction of epichlorohydrin with sodium azide even at a 1:1 molar ratio, decomposed violently when heated to over 150°. The explosive nature of the mixture of products from the butadiene monoxide–sodium azide reaction prevented an absolute proof of structure of these products.

Acknowledgment.—The authors are grateful to the University of Kansas for a University fellowship awarded to R.Y.H. for the completion of this investigation.

LAWRENCE, KANSAS

(26) (a) R. E. Kepner, S. Winstein and W. G. Young, THIS JOURNAL, **71**, 115 (1949); (b) W. G. Young, I. D. Webb and H. L. Goering, *ibid.*, **73**, 1076 (1951).

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

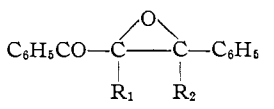
The Rearrangement of α,β-Epoxy Ketones. I. Chalcone Oxides

BY HERBERT O. HOUSE

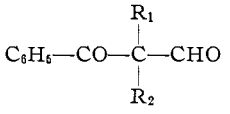
RECEIVED OCTOBER 7, 1953

Four α,β-epoxy ketones have been found to isomerize in the presence of boron trifluoride. In each case the structure of the dicarbonyl compound produced is consistent with the hypothesis that the group which migrates is the one originally bonded to the carbon atom *alpha* to the carbonyl group of the epoxy ketone.

trans-Chalcone oxide (I) has been isomerized to formyldesoxybenzoin (II) by treatment either with aqueous sulfuric acid[1] or with a solution of sulfuric acid in acetic acid.[2] An ethereal solution of boron trifluoride has been found to be a superior agent for effecting this transformation.



I, $R_1 = R_2 = H$



II, $R_1 = H$; $R_2 = C_6H_5$

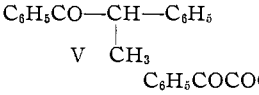
III, $R_1 = H$; $R_2 = CH_3$ IV, $R_1 = CH_3$; $R_2 = C_6H_5$

VI, $R_1 = H$; $R_2 = C_6H_5$ VII, $R_1 = R_2 = C_6H_5$

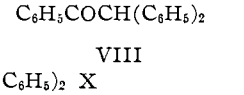
IX, $R_1 = C_6H_5$; $R_2 = H$

In the presence of this catalyst each of the isomeric dypnone oxides III yielded 2-methyl-1,2-diphenyl-1,3-propanedione (IV), isolated as its mono-2,4-dinitrophenylhydrazone. A boiling, ethanolic solution of sodium acetate converted the crude product to α-methyldesoxybenzoin (V); this facile loss of formic acid is in accord with the previous experience of Wittig, Bangert and Kleiner.[3] Similarly, the oxide of β,β-diphenylacrylophenone (VI) afforded 1,2,2-triphenyl-1,3-propanedione (VII), isolated as the deformylated α-phenyldesoxybenzoin (VIII).

Only one of the two possible racemic modifications of α,β-diphenylacrylophenone oxide (IX) could be obtained from the reaction of α,β-diphenylacrylophenone with alkaline hydrogen peroxide. The action of boron trifluoride converted the epoxy ketone IX to phenyl benzhydryl diketone (X) which was isolated as its quinoxaline.



V



VIII

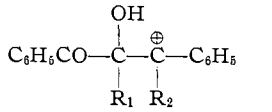
$C_6H_5COCOCH(C_6H_5)_2$ X

(1) J. Algar and J. McKenna, *Proc. Royal Irish Acad.*, **49**, 225 (1944); *C.A.*, **38**, 5502 (1944).

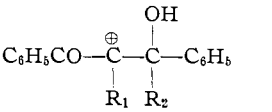
(2) E. Weitz and A. Scheffer, *Ber.*, **54**, 2344 (1921).

(3) G. Wittig, F. Bangert and H. Kleiner, *ibid.*, **61**, 1140 (1928).

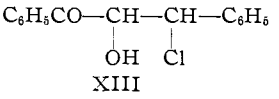
In each case the structure of the dicarbonyl compound produced is consistent with the hypothesis that the group which migrates is the one originally bonded to the carbon atom alpha to the carbonyl group of the epoxy ketone. This result would be predicted by a comparison of the possible ionic intermediates XI and XII.[4] The intermediate XII is especially unfavorable since this structure incorporates adjacent atoms, each bearing at least a partial positive charge.[5]



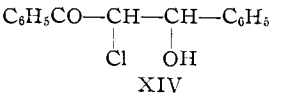
XI



XII



XIII



XIV

The action of stannic chloride in benzene solution Cl on chalcone oxide (I) failed to give a rearranged product, the chlorohydrin XIII being isolated instead. The chlorohydrin XIII was converted to benzyl phenyl diketone, isolated as its quinoxaline, by the method of Baker and Robinson.[6] This transformation has been effected previously by Kohler and Barnes,[7] who did not isolate the intermediate XIII. The action of hydrogen chloride on the oxide I in alcoholic solution has been reported to give the isomeric chlorohydrin XIV.[8,9]

(4) The same argument has been used by Winstein and Henderson [in R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 49] to predict the products obtained when ethylene oxides bearing only alkyl and aryl substituents undergo acid-catalyzed rearrangement.

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 199.

(6) W. Baker and R. Robinson, *J. Chem. Soc.*, 1798 (1932).

(7) E. P. Kohler and R. P. Barnes, THIS JOURNAL, **56**, 211 (1934).

(8) O. Widman, *Ber.*, **49**, 477, 2778 (1916).

(9) Analogous chlorohydrins have been prepared in a related series by H. Jorlander [*Ber.*, **49**, 2782 (1916)].

Experimental[10]

Rearrangement of *trans*-**Chalcone Oxide** (I).—A solution of 0.50 g. of *trans*-chalcone oxide[11,12] in 25 ml. of absolute ether was treated with 5.0 ml. of 45% boron trifluoride in ether. The resulting solution was boiled under reflux for 30 minutes and poured into water. The ether layer was separated, washed with water and then shaken with a saturated aqueous solution of cupric acetate. The copper salt of 1,2-diphenyl-1,3-propanedione, melting with decomposition at 222–223° (lit.[13] 220–221°), was isolated in quantitative yield. A portion of the product was converted to 1,4,5-triphenylpyrazole, m.p. 210.5–211° (lit.[13,14] 210–211°).

Rearrangement of the Dypnone Oxides (III).—The epimeric dypnone oxides were prepared according to the directions of Wasserman, Aubrey and Zimmerman.[15]

(A) **Rearrangement of the** *trans* **Isomer.**—The *trans*-epoxide (m.p. 91.5–93°) was treated with boron trifluoride in the manner described above. The infrared spectrum of the crude product, a viscous oil, was determined in carbon tetrachloride solution. The spectrum exhibits absorption bands at 1670, 1730 and 2720 cm.$^{-1}$, attributable to a conjugated carbonyl group, an unconjugated carbonyl group and the carbon–hydrogen stretching vibration of an aldehyde. The absence of absorption in the region 1400–1435 cm.$^{-1}$ suggests that no hydrogen atoms are bonded to the carbon atoms adjacent to the carbonyl groups. The crude product was converted to its dinitrophenylhydrazone according to the method of Shriner and Fuson.[16] The mono-2,4-dinitrophenylhydrazone of 1,2-diphenyl-2-methyl-1,3-propanedione separated as yellow needles, m.p. 182–183°, yield 0.83 g. (93%). An additional recrystallization from ethanol sharpened the melting point of the dinitrophenylhydrazone to 182.5–183°.

Anal. Calcd. for $C_{22}H_{18}N_4O_5$: C, 63.15; H, 4.34; N, 13.39. Found: C, 63.16; H, 4.52; N, 13.30.

The infrared spectrum[17] of the dinitrophenylhydrazone exhibits the absorption band at 1670 cm.$^{-1}$, attributable to a conjugated carbonyl group, which is also present in the spectrum of the keto-aldehyde.

When a solution of the crude dicarbonyl compound in 60 ml. of ethanol containing 0.4 g. of sodium acetate was boiled under reflux for 3.5 hours and then treated with 2,4-dinitrophenylhydrazine, the 2,4-dinitrophenylhydrazone of α-methyldesoxybenzoin was isolated, m.p. 149–151°, yield 0.76 g. (93%). The pure dinitrophenylhydrazone crystallized from ethanol as orange prisms melting at 150–151°.

Anal. Calcd. for $C_{21}H_{18}N_4O_4$: C, 64.60; H, 4.65; N, 14.35. Found: C, 64.74; H, 4.76; N, 14.40.

The material was identified by comparison with the 2,4-dinitrophenylhydrazone obtained from an authentic sample of α-methyldesoxybenzoin.[18] A mixed melting point showed no depression and the infrared spectra of the two samples are identical.

(B) **Rearrangement of the** *cis* **Isomer.**—Similarly, the *cis*-expoxide (m.p. 160–162°) yielded the mono-2,4-dinitrophenylhydrazone of 1,2-diphenyl-2-methyl-1,3-propanedione, m.p. 182–183°, in quantitative yield. The dinitrophenylhydrazones obtained from the *cis* and *trans* isomers of dypnone oxide were identified both by a mixed melting point determination and by comparison of their infrared spectra.

Rearrangement of β,β-Diphenylacrylophenone Oxide (VI).—β,β-Diphenylacrylophenone oxide was prepared by the method of Kohler, Richtmyer and Hester.[19] The infrared spectrum[17] of the epoxide exhibits an absorption band at 1695 cm.$^{-1}$, attributable to a carbonyl group; the ultraviolet spectrum has an absorption peak at 252 mμ (ϵ_{max} 14,600). When treated with boron trifluoride the epoxy ketone was isomerized to a viscous oil. In the 3 and 6 μ regions the infrared spectrum[20] of this crude product was remarkably similar to the spectrum of the rearrangement products obtained from the dypnone oxides, absorption bands occurring at 1670, 1730 and 2730 cm.$^{-1}$. A boiling, ethanolic solution of sodium acetate converted the crude ketoaldehyde to α-phenyldesoxybenzoin, m.p. 134.5–136°, yield 0.37 g. (80%). The pure ketone crystallized from an ethanol-water mixture as white needles melting at 135–136° (lit.[21] 136–137°).

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.21; H, 5.92. Found: C, 88.07; H, 6.13.

The infrared spectrum[17] of the compound exhibits an absorption band at 1680 cm.$^{-1}$, attributable to a conjugated carbonyl group. However, the ketone failed to form an oxime under the usual conditions.[22]

α,β-Diphenylacrylophenone Oxide (IX).—A solution of 5.00 g. of α,β-diphenylacrylophenone[23] in 125 ml. of methanol, cooled in a water-bath, was treated with a mixture of 10 ml. of 30% hydrogen peroxide and 10 ml. of 6 *N* aqueous sodium hydroxide. The mixture was stirred for 3 hours, diluted with 100 ml. of water and filtered with suction. The crude product crystallized from methanol as white prisms, m.p. 82–83.5°, yield 3.26 g. (61.7%). An additional recrystallization from the same solvent afforded the pure oxide melting at 82.5–83.5°.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.07; H, 5.26.

The infrared spectrum[20] of the oxide contains an absorption band at 1680 cm.$^{-1}$, attributable to a conjugated carbonyl group; the ultraviolet spectrum exhibits an absorption peak at 252 mμ (ϵ_{max} 16,000).

Rearrangement of α,β-Diphenylacrylophenone Oxide, (IX).—The epoxide was treated with boron trifluoride in the usual manner. The infrared spectrum[20] of the crude product, a deep yellow liquid, exhibits two strong absorption bands in the 6 μ region, one at 1680 cm.$^{-1}$ and the other at 1710 cm.$^{-1}$, suggestive of an α-diketone structure. The diketone was isolated as its quinoxaline, m.p. 195.5–198.5°, in quantitative yield. The pure product crystallized from ethanol as white needles melting at 198–199°. The material was compared with an authentic sample of 2-phenyl-3-benzhydrylquinoxaline, prepared according to the method of Kohler and Weiner.[24] A mixed melting point showed no depression and the infrared spectra of the two samples are identical. The ultraviolet spectrum of the quinoxaline exhibits absorption peaks at 240 mμ (ϵ_{max} 40,300) and at 326 mμ (ϵ_{max} 9,900).

3-Chloro-2-hydroxy-1,3-diphenylpropanone (XIII).—A solution of 1.00 g. of chalcone oxide in 50 ml. of dry benzene was treated with 1.2 ml. of stannic chloride. After the mixture had been stirred for 15 minutes, it was poured into 100 g. of ice. The benzene layer was separated, washed with water and the solvent removed under an air blast. The residue crystallized from petroleum ether (b.p. 90–100°) in white prisms, m.p. 70–72°, yield 0.85 g. (72%). An additional recrystallization from hexane afforded the pure chlorohydrin, m.p. 71–72°.

Anal. Calcd. for $C_{15}H_{13}ClO_2$: C, 69.12; H, 5.03; Cl 13.60. Found: C, 69.09; H, 5.12; Cl, 13.40.

The infrared spectrum[20] of the compound exhibits a strong absorption band at 1700 cm.$^{-1}$, attributable to a carbonyl group, as well as a relatively sharp band at 3450 cm.$^{-1}$, attributable to a hydroxyl group. The same compound was produced when an ether solution of the epoxide was saturated with hydrogen chloride. A boiling, ethanolic solution of sodium acetate converted the chlorohydrin to benzyl

(10) All melting points are corrected. The infrared spectra were determined with a Baird double beam infrared recording spectrophotometer, model B, fitted with a sodium chloride prism. The ultraviolet spectra were all determined in ethanol solution with a Cary ultraviolet recording spectrophotometer, model 11 MS. The microanalyses were performed by Dr. S. M. Nagy and his associates.

(11) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

(12) H. H. Wasserman and N. E. Aubrey, Abstracts of Papers, 124th Meeting of the American Chemical Society, p. 16-O, Chicago, Ill., September, 1953.

(13) W. Wislicenus and A. Ruthing, *Ann.*, **379**, 229 (1911).

(14) A. H. Blatt, THIS JOURNAL, **60**, 1164 (1938).

(15) H. H. Wasserman, N. E. Aubrey and H. E. Zimmerman, *ibid.*, **75**, 96 (1953).

(16) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

(17) Determined in Nujol mull.

(18) Bruzau, *Ann. chim.*, [11] **1**, 257 (1934).

(19) E. P. Kohler, N. K. Richtmyer and W. F. Hester, THIS JOURNAL, **53**, 205 (1931).

(20) Determined in carbon tetrachloride solution.

(21) M. S. Newman and A. Katner, THIS JOURNAL, **73**, 4199 (1951).

(22) E. P. Kohler, *Am. Chem. J.*, **36**, 177 (1906).

(23) E. P. Kohler and E. M. Nygaard, THIS JOURNAL, **52**, 4128 (1930).

(24) E. P. Kohler and N. Weiner, *ibid.*, **56**, 434 (1934).

phenyl diketone which was isolated as 2-phenyl-3-benzylquinoxaline, m.p. 96–97° (lit. 97–98°,[25] 98–99°[8]). The ultraviolet spectrum of the quinoxaline closely resembles the spectrum of 2-phenyl-3-benzhydrylquinoxaline, absorption peaks occurring at 240 mμ (ϵ_{max} 35,000) and 324 mμ (ϵ_{max} 10,000).

(25) T. L. Jacobs, THIS JOURNAL, **58**, 2272 (1936).

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MAINE]

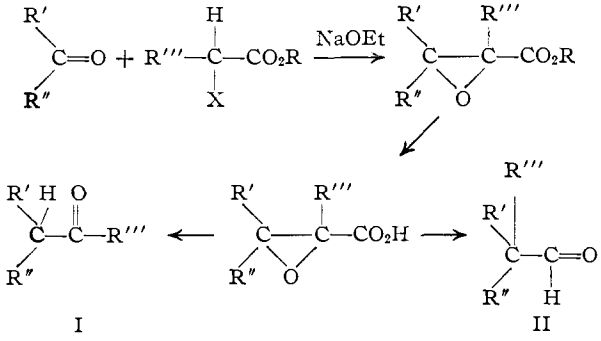
The Synthesis and Reactions of Certain α-Substituted Glycidic Esters

BY HORTON H. MORRIS AND MARGARET L. LUSTH[1]

RECEIVED SEPTEMBER 23, 1953

Several α-substituted glycidic esters, ethyl α-*n*-alkyl-α,β-epoxycyclohexylideneacetates, have been prepared. Saponification of these esters and decarboxylation of the resulting glycidic acids gave ketones as primary products, as proved by alternate synthesis, mixed melting points of derivatives and attempted oxidation. Contrary to an earlier report, ethyl α-*n*-decyl-α,β-epoxycyclohexylideneacetic acid decarboxylated to yield 1-cyclohexyl-1-undecanone instead of α-*n*-decylcyclohexanecarboxaldehyde. An important side reaction in the preparation of these glycidic esters was found to be the saponification of a portion of the glycidic ester during the course of the reaction, the resulting acid material accounting for over 40% of the yield in one case.

The condensation of an aldehyde or ketone with an α-halo ester, in the presence of a basic condensing agent, yields an α,β-epoxyester (glycidic ester). The reaction is of interest since it provides a route to aldehydes or ketones of greater complexity than those used in the original condensation.



I II

Darzens has reported[2] that glycidic acids with higher molecular weight α-substituents, in particular *n*-decyl, rearrange on decarboxylation to form tertiary aldehydes of the type II. It has been shown[3a,b] that if the α-substituent is methyl, ethyl, *n*-butyl or *n*-hexyl, a ketone of the type I results. In order to determine at what point between *n*-hexyl and *n*-decyl the rearrangement to aldehyde takes place, an homologous series of glycidic esters (ethyl α-*n*-alkyl-α,β-epoxycyclohexylideneacetates) with α-substituents of methyl through *n*-decyl was prepared from cyclohexanone and α-bromo esters, using sodium ethoxide as the condensing agent. The glycidic esters with α-substituents of *n*-butyl and *n*-hexyl were reported in a previous article[3b] from this Laboratory and are not included here. The esters were saponified and the resulting acids decarboxylated by heating for three or four hours at atmospheric pressure. The decarboxylation products in every case were ketones, as shown by alternate synthesis, mixed melting points of derivatives and oxidation studies. Evidently Darzens was misled by the fact that a small amount of an oxidizable contaminant present in the decarboxylation products gives aldehyde color tests.

In order to prove the structure of the decarboxylation products, a series of cyclohexyl ketones were prepared by the following methods. The ethyl, *n*-propyl and *n*-amyl cyclohexyl ketones were obtained by use of a modified Friedel–Crafts type acylation as adapted from the procedure reported by Nenitzescu and Cioranescu.[4] The *n*-heptyl, *n*-octyl and *n*-decyl cyclohexyl ketones were prepared by means of a condensation of the appropriate di-*n*-alkylcadmium compound and cyclohexanecarboxyl chloride, following a procedure given by Cason.[5] Semicarbazones and 2,4-dinitrophenylhydrazones were prepared from these ketones and mixed melting points determined with the corresponding products obtained from the decarboxylation of the glycidic acids. No depression of the melting point was observed in any case.

In order further to establish the structure of the decarboxylation product from α-*n*-decyl-α,β-epoxycyclohexylideneacetic acid and to attempt to find an explanation for the fact that the material gave aldehyde color tests, a sample was subjected to oxidation with aqueous permanganate. Less than 15% of the material could be oxidized. Repetition of the oxidation, using acetone as solvent, gave essentially the same results.

There seems to be no doubt that ketones will result on the decarboxylation of α-substituted glycidic acids when the α-substituent is an alkyl group. Glycidic esters, however, have occasionally been reported to rearrange to α-keto esters on heating, and such esters would be expected to yield aldehydes on decarboxylation. Such a rearrangement may have occurred in the case reported by Darzens, and would account for the results he obtained. Preliminary evidence indicates that this is not the case, but the possibility is being checked.

The preparation of the condensing agent in the

(1) From the thesis submitted by M. L. Lusth in partial fulfillment of the requirements of the degree of Master of Science in Chemistry, June, 1953. Presented before the Division of Organic Chemistry at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 9, 1953.

(2) G. Darzens, *Compt. rend.*, **195**, 884 (1932).

(3) (a) M. Mousseron and R. Granger, *ibid.*, **218**, 358 (1944); M. Mousseron, *et al.*, *Bull. soc. chim. France*, 598 (1947); (b) N. K. Nelson and H. H. Morris, THIS JOURNAL, **75**, 3337 (1953).

(4) C. D. Nenitzescu and E. Cioranescu, *Ber.*, **69**, 1820 (1936).

(5) J. Cason, THIS JOURNAL, **68**, 2078 (1946).