To this mixture was then added the pyridine solution of the epoxyalcohol and the mixture was allowed to stand at room temperature for 16 hr. The mixture was then diluted with water and ether extracted after acidification with hydrochloric acid. The ether layer was washed with water and then dilute sodium bicarbonate. The latter extract was acidified with dilute hydrochloric acid and ether extracted. This extract was dried over sodium sulfate and concentrated. The residue weighed 70 mg. and melted at 111–114°. Its infrared spectrum was identical to that of the glycidic acid obtained from the Darzens reaction of benzaldehyde and ethyl α-chlorophenylacetate followed by saponification.

Lithium Aluminum Hydride Reduction of Ethyl 2,3-*cis*-Diphenylglycidate.—To a solution of 1.0 g. (0.0037 mole) of ethyl 2,3-*cis*-diphenylglycidate, m.p. 58.0–59.0°, in a flask equipped with magnetic stirring bar, dropping funnel, reflux condenser and drying tube was added 4.50 ml. of 0.44 molar lithium aluminum hydride solution. After five minutes, excess lithium aluminum hydride was decomposed by addition of water dropwise until a precipitate of aluminum hydroxide separated. The solution was filtered and concentrated *in vacuo*. After one crystallization from chloroform–hexane there was obtained 0.30 g. of product, m.p. 116.0–117.0°. The infrared spectrum of this material was identical with that of previously prepared 2,3-*cis*-diphenyl-2,3-epoxypropan-1-ol. The material in the filtrates was found by infrared analysis to contain unreacted starting ester.

2,3-*trans*-Diphenylprop-2-ene-1-ol.—The following is a slight modification of the procedure of Lutz.[30] To a solution of 1.00 g. (0.0045 mole) of α-phenyl-*cis*-cinnamic acid, m.p. 137°, in 40 ml. of anhydrous ether in a 100-ml. flask fitted with reflux condenser, sodium hydroxide drying tube, magnetic stirrer, dropping funnel and Glas-col heater was added over 5 minutes 20.0 ml. of a 0.44 molar lithium aluminum hydride solution in ether. During the addition and for an additional 50 min. the mixture was stirred and refluxed gently by means of external heating. Then water was added dropwise until a precipitate of alumina separated. The solution was diluted with ether and filtered. The filtrate was concentrated *in vacuo* leaving 0.70 g. of oil which later solidified to a solid of m.p. 67–70°. This was crystallized from hexane several times with negligible loss to the filtrate, affording 2,3-*trans*-diphenylprop-2-ene-1-ol, m.p. 73.0–74.0° (reported[30] 73–74°). The infrared spectrum of this compound differed considerably from that of its stereoisomer.

2,3-*trans*-Diphenyl-2,3-epoxypropan-1-ol.—A solution of 0.691 g. of 2,3-*trans*-diphenylprop-2-ene-1-ol, prepared as described above, in 30 ml. of chloroform was added 0.50 g. of sodium acetate and 1.50 ml. of 40% (Becco) peracetic acid solution in acetic acid. This mixture was allowed to remain at room temperature for 22 hr. The chloroform solution was then washed with water, dried over anhydrous potassium carbonate and concentrated *in vacuo* to leave 0.371 g. of oil which solidified. The infrared spectrum of this material showed it to be only slightly impure product. The material was then chromatographed on a 19 × 490 mm. silica gel column packed with 5% ether in hexane. Six fractions of 100 ml. each were obtained by elution with 10% ether in hexane. Fractions 7 through 18 were obtained with 15% ether in hexane. Only fractions 11 through 15 contained appreciable quantities of material; the weights and melting points were: fraction 11, 49.7 mg., m.p. 45–47°; fraction 12, 59.7 mg., m.p. 48.0–49.0°; fraction 13, 62.1 mg., m.p. 47.5–49.0°; fraction 14, 46.9 mg., m.p. 47.0–48.0°; fraction 15, 21.6 mg., m.p. 43.0–47.0°. These fractions were combined and crystallized once from aqueous methanol to yield 112.9 mg. of 2,3-*trans*-diphenyl-2,3-epoxypropan-1-ol, m.p. 50–52°, whose infrared spectrum was that of the pure material obtained previously by sodium borohydride reduction of the corresponding epoxyaldehyde.

Acknowledgment.—We wish to thank the Alfred P. Sloan Foundation for support of a postdoctoral fellowship for B. S. Thyagarajan. Also we would like to express our appreciation to the Office of Ordnance Research, U. S. Army, for a summer research assistantship for L. Singer.

EVANSTON, ILL.

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(30) R. E. Lutz and E. H. Rinker, Jr., THIS JOURNAL, **77**, 368 (1955).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

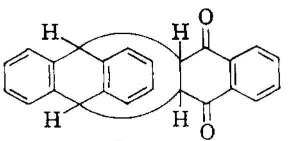
The *cis* and *trans* 12-Benzoyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acids

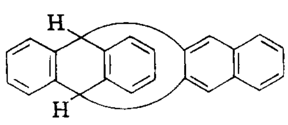
BY CHARLES D. HURD AND ALBERT TOCKMAN

RECEIVED MAY 28, 1958

The *trans* acid III, prepared by reaction of benzene and aluminum chloride with the adduct of anthracene and maleic anhydride, does not cyclize to a diketone even when forced. The same *trans* isomer was made from the adducts of anthracene and benzoylacrylic acid (*cis* or *trans*) or fumaric ester. The *cis* isomer VI was prepared starting with the adduct of anthracene and methyl acetylenedicarboxylate; VI changed to III on alkaline treatment. Other adducts of anthracene that were studied included those of *trans*-dibenzoylethylene and *trans*-styrylacetic acid. Sodium borohydride was an efficient reducing agent toward the ketone function of III, whereas other methods of reduction failed.

The adduct of anthracene and 1,4-naphthoquinone (I) was examined unfruitfully in earlier work[1] as a source of 5,12-dihydro-5,12-*o*-benzenonaphthacene (II); but the conversion of I into II was not pursued exhaustively, in view of the successful synthesis of II by other methods.


I


II

In planning to test another synthesis of I, namely, by cyclization of 12-benzoyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid (III), we found that III had already been described by Barnett[2] and co-workers and that these investigators were unable to bring about such a cyclization. They prepared III by Friedel–Crafts reaction of benzene with the adduct of anthracene and maleic anhydride. They did not elaborate on their statement that compound I could not be made from III. The benzoyl carbonyl would, of course, deactivate the phenyl part of this radical toward electrophilic attack, but this should be no more true than in the benzoyl group of *o*-benzoylbenzoic acid which readily yields anthraquinone.

A more fundamental reason for non-formation of I from III is that III may be of *trans* structure,

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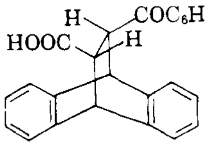
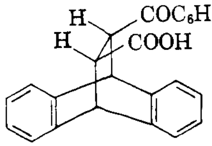
(1) C. D. Hurd and L. H. Juel, THIS JOURNAL, **77**, 601 (1955).

(2) E. B. Barnett, N. F. Goodway, A. G. Higgins and C. A. Lawrence, *J. Chem. Soc.*, 1224 (1934). The m.p. was listed as 234°. Its empirical formula was given as $C_{20}H_{18}O_3$, but it should have been $C_{24}H_{18}O_3$.

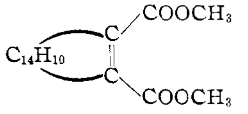
whereas a *cis* structure would be necessary for cyclization. Accordingly, the stereochemistry of III and related substances was investigated.

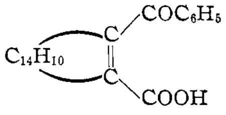

III


VI

Our difficulties started as soon as we attempted to duplicate Barnett's product. Instead of obtaining a material melting at 234°, ours which analyzed correctly for III melted with decomposition at 246°. To check this synthesis we prepared it in several other ways: namely, from anthracene and *trans*-benzoylacrylic acid, from anthracene and *cis*-benzoylacrylic acid, and from anthracene and methyl (or ethyl) fumarate followed by conversion of the adduct to the half acid chloride and then reaction with benzene and aluminum chloride. Identical products were obtained from all of these approaches.

The same product (m.p. 245°) was obtained in a still different synthesis, starting with anthracene and methyl acetylenedicarboxylate. This approach maintained compounds of *cis* structure in the several steps, and it is of interest to record that a lower-melting stereoisomeric form was obtained prior to the change to the higher-melting isomer. In this experiment, the *cis* adduct IV was hydrolyzed and converted (with acetic anhydride) to the cyclic acid anhydride, also necessarily *cis*. The last compound was treated with benzene and aluminum chloride, forming *cis* keto acid V. Hydrogenation of V in alkaline solution with Raney nickel alloy yielded VI (m.p. 234–235°), the *cis* isomer of III; VI was changed into III (m.p. 245°) by heating it with alcoholic potassium hydroxide, thus demonstrating that III must be *trans*.


IV


V

On first thought, one might imagine that our VI was the same as Barnett's acid of m.p. 234° but we are convinced that this is not true. Instead, it is simply fortuitous that the *cis* acid melts at 234–235°. We have no suggestions to explain the difference in melting points of Barnett's acid and our *trans*-acid.

It is noteworthy that both *trans* and *cis* samples of benzoylacrylic acid gave the same product (III). Lutz[3] obtained *trans*-benzoylacrylic acid by reaction of benzene, maleic anhydride and aluminum chloride. This means either that the *trans* product was formed directly, or if the *cis* adduct was obtained first that it rearranged to *trans* while being processed. Colorless *cis*-benzoylacrylic acid is known[4] to change to the more stable *trans* isomer by the action of dilute hydrochloric acid, dilute sodium carbonate, fusion, or by sunlight on a chloroform solution containing a trace of iodine.

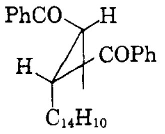
Similarly, although the *trans*-III is formed from benzene, aluminum chloride and the *cis* anthracene–maleic adduct, it is an open question whether *trans*-III is formed directly or whether it arises from *cis*-VI during processing. The rearrangement of VI to III under the influence of a proton (or $AlCl_3$) follows the usual steps of protonation at the carbonyl group, deprotonation to the enol, then tautomerization.

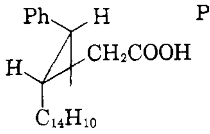
Several reactions of III were studied. The amide, the methyl ester and the ethyl ester were prepared by conventional methods. In keeping with the assignment of *trans* structure and in agreement with Barnett's report we were unable to bring about cyclization by acids. Most of it was recoverable after heating (100°, 30 min.) with polyphosphoric acid, or by treatment in hot benzene with phosphorus pentachloride. Other reagents tested without causing cyclization of III were sulfuric acid, stannic chloride, aluminum chloride.

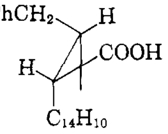
Three reduction reactions, namely, Wolff–Kishner, Clemmensen and Meerwein–Ponndorf–Verley, were unsuccessful with III. Either there was non-reaction as with the last, essentially non-reaction with the second, or dissociation of the adduct because of high temperature as with the first; but the Clemmensen reduction did yield a small amount of uncharacterizable material.

Sodium borohydride was an efficient reducing agent for esters of III, the keto esters changing to the corresponding hydroxy esters. These γ-hydroxy esters showed no tendency to change into lactones, again confirming the *trans* structure assigned to them.

The adduct VII of anthracene and *trans*-dibenzoylethylene was prepared with the intention of preparing it also by reaction of the acyl chloride of III with benzene and aluminum chloride, but this reaction was unsuccessful.


VII


VIII


IX

Another synthesis of a related nature was the addition of *trans*-styrylacetic acid, $C_6H_5CH{=}CHCH_2COOH$, to anthracene at 255° giving a compound presumably of structure VIII, 12-phenyl-9,10-dihydro-9,10-ethanoanthracene-11-acetic acid. A small amount of lower melting isomer was found also among the products. Since it seems unlikely that this is a *cis* isomer of VIII it is suggested that the compound is 12-benzyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid (IX), formed as a result of partial isomerization of the styrylacetic acid at the elevated temperature to 4-phenylcrotonic acid, $PhCH_2CH{=}CHCOOH$.

Experimental

All melting points are corrected. They were taken on a block, calibrated throughout its entire range with known reference compounds. The microanalyses were performed by Mrs. C. White, Miss J. Sorensen and Miss Hilda Beck.

12-Benzoyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid (III). 1. From Maleic Anhydride.[2]—Ten grams of the adduct (m.p. 266° dec.) of anthracene and

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[3] R. E. Lutz, This Journal, **52**, 3423 (1930).

[4] R. E. Lutz and G. W. Scott, *J. Org. Chem.*, **13**, 284 (1948).

maleic anhydride, 11 g. of aluminum chloride and 100 ml. of benzene were heated together on a steam-bath for one hour. When cool, the reaction mixture was decomposed with ice and hydrochloric acid and the solvent recovered by steam distillation. The crude product obtained by filtration was dissolved in 250 ml. of warm 5% aqueous sodium hydroxide solution, treated with Norit, filtered and acidified. The crude yield after filtration and drying averaged 12.5 g. (97%). After several crystallizations from about 1.5 liters of toluene, pure III was obtained. It melted at 246° dec. to an orange oil. It fluoresced in ultraviolet light.

Anal. Calcd. for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.58; H, 5.19.

The infrared absorption of this compound, taken on a saturated solution of it in chloroform, showed twin absorption peaks at 5.80, 5.95 μ which is consistent for a structure containing an unconjugated keto acid. The same acid of m.p. 246° was obtained also when the crude reaction product was processed without use of sodium hydroxide.

2. **From *trans*-Benzoylacrylic Acid.**—A mixture of 5 g. of yellow, *trans*-benzoylacrylic acid,[5] 5 g. of anthracene and 50 ml. of toluene was refluxed for 2 hours, at which time colorless crystals of the adduct began to separate. After another hour of refluxing, the mixture was cooled and filtered; yield 7.0 g. (70%). After two recrystallizations from toluene, the m.p. was 247° dec.; mixed m.p. with that from preparation (1), 246–247°.

3. **From *cis*-Benzoylacrylic Acid.**—A mixture of 2.5 g. of this colorless *cis* acid,[4] m.p. 85°, 2.5 g. of anthracene and 25 ml. of toluene became yellow immediately, and after 3 hours of refluxing 3.5 g. (70%) of a white adduct was collected on a filter. It was recrystallized. Its m.p. and mixed m.p. was 246° dec.

Similar reaction (and coloring) was noticed if benzene was the solvent in place of toluene, but there was no reaction or yellowing if acetone was the solvent.

4. **From Methyl Fumarate.**—The adduct of methyl fumarate to anthracene was prepared, following directions of Bachmann and Scott[6] by refluxing the mixture of reactants for 72 hours in dioxane solution. To purify the adduct, we found the following procedure to be easier than the method given in the literature: water was added, the dioxane was removed by distillation at atmospheric pressure, and the insoluble residue was separated and recrystallized from methanol; m.p. 106°, as reported.

This diester (13.5 g.) was half saponified by refluxing it for 4 hours in 100 ml. of methanol that contained 2.5 g. of potassium hydroxide, then diluting it with 200 ml. of water, and acidifying. The 6.5 g. of precipitated methyl hydrogen 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate[7] was recrystallized from methanol; m.p. 205° dec.

Anal. Calcd. for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.66; H, 5.53.

The carboxyl of the half ester (6.5 g.) was converted to the acyl chloride by refluxing for half an hour with thionyl chloride (5 ml.), after which the excess of thionyl chloride was removed under diminished pressure. To the residue was added 100 ml. of benzene and 5.5 g. of aluminum chloride. After gentle refluxing for one hour, the reaction mixture was decomposed with ice and hydrochloric acid. Seven grams of brown solid was isolated by filtration after the benzene had been removed by steam distillation. The product was decolorized in 50% acetic acid with carbon and was crystallized from ligroin and ethyl acetate. The pure keto ester melted at 133–134° and was identical to the methyl ester formed by direct esterification of III (see below). One gram of the ester was saponified by refluxing with 1 g. of potassium hydroxide and 10 ml. of ethyl alcohol for 5 hours. The suspension was added to an excess of acidulated water and the resultant solid collected by filtration; m.p. (and mixed m.p. with samples from procedures 1 and 2), 245°.

5. **Initial Step Toward Synthesis from Ethyl Fumarate. Ethyl 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylate.**—A mixture of 28 g. of anthracene, 35 g. of ethyl fumarate and 150 ml. of dioxane was refluxed for 60 hours. Water was added and the dioxane was removed by distillation. The residue was chilled and the water removed by decantation. The residue was recrystallized from methyl alcohol to give 55 g. of adduct which melted at 107°.

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.40; H, 6.33. Found: C, 74.94; H, 6.17.

6. **From Methyl Acetylenedicarboxylate.**—The adduct of anthracene and methyl acetylenedicarboxylate was prepared and converted to the cyclic acid anhydride, following directions[8] of Diels and Alder; m.p. 255° dec. (lit. m.p. 248°). This material (11 g.) was placed in reaction with benzene (150 ml.) and aluminum chloride (11 g.) for one hour at reflux temperature to yield **12-benzoyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxylic acid** (14 g.) (V). This substance was crystallized from both ethanol and benzene but either procedure resulted in material containing one mole of solvent of crystallization. Both products melted at 150° with evolution of gas. The products turned yellow on heating or after several hours of exposure to light. Starting with either solvate, all attempts to prepare solvent-free compound by warming in a vacuum oven gave material with an inconsistent, wide-range melting point. Some values observed were 120–140°, 130–145° and 140–155°, all with decomposition.

Anal. (from ethyl alcohol). Calcd. for $C_{24}H_{16}O_3 \cdot C_2H_5$-OH: C, 78.39; H, 5.57; neut. equiv., 398. Found: C, 78.07; H, 5.71; neut. equiv., 394. (From benzene) Calcd. for $C_{24}H_{16}O_3 \cdot C_6H_6$: C, 83.70; H, 5.15. Found: C, 83.27; H, 5.16.

To a stirred solution of 2.0 g. of V (recrystallized from ethanol) and 6.0 g. of sodium hydroxide in 60 ml. of water at 60°, there was added in small portions 6.0 g. of Raney nickel catalyst alloy[9]; the evolution of hydrogen caused much foaming. The reaction mixture was stirred for one hour after the addition was complete and filtered while warm into an excess of concentrated hydrochloric acid. The product obtained was dried and crystallized from toluene. When pure this *cis* form, VI, melted at 234–235° dec.

To rearrange VI to III the former was refluxed for one day with 2 g. of potassium hydroxide in 20 ml. of ethyl alcohol. The reaction mixture was added to an excess of acidulated water and the resultant solid was separated by filtration. On recrystallization from toluene, the acid melted at 245° dec. to an orange-colored oil; its melting point was not depressed by the addition of above samples of III.

Derivatives of III. Amide.—The amide was prepared by heating 1 g. of III with 5 ml. of thionyl chloride for 20 minutes. The reaction mixture was poured into ice-cold ammonium hydroxide. The 1 g. of crude product was collected, dried and crystallized from toluene. An analytical sample turned purple before melting and melted at 260° to a purple oil.

Anal. Calcd. for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42. Found: C, 81.50; H, 5.36.

The III used above was prepared by methods 1 or 2 and the amides from the two sources were identical.

Ethyl Ester.—The acid chloride, as prepared above using thionyl chloride, was mixed with an excess of absolute ethanol. Then water was added and the precipitated ester was crystallized several times from methanol–water; m.p. 129°.

Anal. Calcd. for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.42; H, 5.77.

Methyl Ester.—A mixture of 250 ml. of methanol, 2.5 ml. of concd. sulfuric acid and 10 g. of III (made by methods 1 and 4) was refluxed for 12 hours and then was added to a stirred, dilute aqueous solution of sodium bicarbonate. Ten grams of the crude ester was collected by filtration and dried. After several crystallizations from ethyl acetate containing about 10% ligroin (b.p. 85–100°) the ester melted at 133–134° dec.

Anal. Calcd. for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47. Found: C, 81.35; H, 5.46.

Reduction. Methyl 12-(α-Hydroxybenzyl)-9,10-dihydro-9,10-ethanoanthracene-11-carboxylate.—One gram of the methyl ester of III was heated with 0.2 g. of sodium borohydride in 50 ml. of alcohol until solution occurred. After standing for several hours, the reaction mixture was poured

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(5) O. Grummitt, E. Becker and C. Miese, *Org. Syntheses*, **29**, 11 (1949).

(6) W. E. Bachmann and L. Scott, THIS JOURNAL, **70**, 1458 (1948).

(7) This half ester, m.p. 209–210°, was prepared recently by H. M. Walton, *J. Org. Chem.*, **22**, 308 (1957).

(8) O. Diels and K. Alder, *Ann.*, **486**, 191 (1931).

(9) D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942).

into an excess of slightly acidulated water and the resultant gram of solid was collected on a filter. After drying and several recrystallizations from ligroin the hydroxy ester melted at 161–162° dec.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 81.05; H, 5.99. Found: C, 81.46; H, 5.89.

Ethyl 12-(α-Hydroxybenzyl)-9,10-dihydro-9,10-ethanoanthracene-11-carboxylate.—One gram of the ethyl ester of III was warmed on the steam-bath for 10 minutes with 0.2 g. of sodium borohydride in 20 ml. of ethyl alcohol. The product was precipitated by the addition of water and crystallized as the monohydrate from dilute alcohol; it melted at 77° dec. When dried for 24 hours at 60° and 10 mm., the anhydrous compound was obtained, m.p. 126°. It depressed the melting point of ethyl 12-benzoyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylate (m.p. 129°) by thirty or forty degrees.

Anal. (of hydrate) Calcd. for $C_{26}H_{24}O_3 \cdot H_2O$: C, 77.58; H, 6.51. Found: C, 77.79; H, 6.47. (Anhydrous material) Calcd. for $C_{26}H_{24}O_3$: C, 81.23; H, 6.29. Found: C, 81.24; H, 5.96.

11,12-Dibenzoyl-9,10-dihydro-9,10-ethanoanthracene.—*trans*-Dibenzoylethylene, m.p. 110°, was prepared from fumaryl chloride, benzene and aluminum chloride by the method of Conant and Lutz.[10]

Three grams of each of *trans*-dibenzoylethylene and anthracene were fused together at 200° for 5 minutes. Crystallization of the crude product from benzene–ligroin gave: (a) 1.0 g. of anthracene, (b) 2.0 g. of adduct melting 153–161°, and (c) 1.5 g. more material from which an additional gram of adduct was obtained on recrystallization from alcohol. The analytical sample was recrystallized several times from alcohol and melted 163–164°.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 87.07; H, 5.22.

12-Phenyl-9,10-dihydro-9,10-ethanoanthracene-11-acetic Acid (X).—*trans*-Styrylacetic acid, m.p. 88°, was made from phenylacetaldehyde and malonic acid following both of two reported procedures.[11]

Seven grams of this *trans* acid and 14 g. of anthracene were fused at 220–230° for 5 hours. After cooling the mixture the solid mass was pulverized and extracted twice with hot 5% aqueous sodium carbonate solution. Unreacted anthracene was removed by filtration. Acidification of the filtrate yielded a mixture of solid acids which was treated with 50% acetic acid. This treatment caused solution of the unreacted styrylacetic acid without dissolving the adduct. The latter was dissolved in hot toluene and on cooling an acid separated; yield 4.0 g. (27%), m.p. 267° dec. The filtrate was processed for an isomeric acid (below).

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.88. Found: C, 84.30, 85.02; H, 6.08, 6.00.

The same product was formed but in lower yields if solvents (toluene or *o*-dichlorobenzene, both at reflux temperature) were employed.

The Lower Melting Adduct, Presumably 12-Benzyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid (XI).—The filtered solution of toluene from the previous run was combined with filtrates of two other analogous runs and the total was evaporated. The residue weighed about 0.5 g. It was crystallized from benzene; m.p. 212° dec. Neither the higher or the lower melting adducts could be isomerized by refluxing for 6 hours in toluene or by boiling alcoholic potassium hydroxide, which means that X and XI were not *cis–trans* isomers.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.88. Found: C, 84.98; H, 6.13.

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[10] J. Conant and R. Lutz, THIS JOURNAL, **45**, 1303 (1923).

[11] D. Vorländer and E. Strunck, *Ann.*, **345**, 233 (1906); R. Linstead and L. Williams, *J. Chem. Soc.*, 2735 (1926).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE STATE UNIVERSITY]

Epoxyethers. XVII.[1] Synthesis from an α-Chloro-β-hydroxyether[2]

BY CALVIN L. STEVENS AND ROBERT L. MCLEAN

RECEIVED JULY 28, 1958

The α-hydroxyketal I has been used as a starting material for the synthesis of the epoxyether III in 83% yield. The key intermediate in this synthesis was the α-chloro-β-hydroxyether II prepared from I and trichloroacetyl chloride. The *p*-nitrobenzoate and 3,5-dinitrobenzoate esters of the α-hydroxyketal I were converted by acetyl chloride to the corresponding α-chloroether derivatives VI and VII in excellent yield. Treatment of these derivatives with liquid ammonia or sodamide in ether did not remove the protecting ester group, but rather led to the formation of nitrogen-containing products which were formulated as methoxy oxazolines VIII and IX.

Epoxyethers have been prepared easily from many α-halocarbonyl compounds by reaction with alkoxide ion.[3] The one main limitation of this preparation is that when a Favorski rearrangement is possible, an α-haloketone will undergo this rearrangement in many cases to the exclusion of epoxyether formation.[4] A vinyl ether has been converted to an epoxyether by oxidation with an organic peracid, but special precautions were necessary[5] since the organic acid that was formed reacted readily with the epoxyether. Since α-hydroxyketals can be prepared corresponding to the α-bromoketones that undergo the Favorski rearrangement,[6] the object of this investigation was the preparation of an epoxyether from a corresponding α-hydroxyketal.[7]

The essential feature of this preparation was the conversion of a ketal to an α-chloroether by an acid chloride as reported by Straus and Heinze[8] in 1932. As applied to the α-hydroxyketal in this investigation the resulting α-chloroether was at once a chlo-

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[1] Paper No. XVI in the Epoxyether series appears in THIS JOURNAL, **80**, 4072 (1958).

[2] Sponsored in part by the Office of Ordnance Research, U. S. Army, and in part by Grant No. A-769 from the National Institute of Arthritis and Metabolic Diseases, Public Health Service.

[3] The preparations of epoxyethers from various phenyl ketones have been published in THIS JOURNAL, **72**, 4758 (1950); **74**, 618 (1952); **75**, 3977 (1953); **76**, 718 (1954); **77**, 5412 (1955). The preparation from α-haloaldehydes appears in **76**, 2695 (1954) and **79**, 3448 (1957). The reaction of α-halotrimethyl cyclohexanone with alkoxide ion to form a bicycloepoxyether appears in **80**, 4072 (1958).

[4] R. B. Loftfield and L. Shaw discuss the possible control of the ratio of these reaction products in *ibid.*, **76**, 35 (1954).

[5] C. L. Stevens and J. Tazuma, *ibid.*, **76**, 715 (1954).

[6] *Cf.* C. L. Stevens and A. E. Sherr, *J. Org. Chem.*, **17**, 1228 (1952), for synthesis in the diphenylacetone series.

[7] An α-hydroxy diisopropylketal has been shown to lose isopropyl alcohol in the presence of an acid catalyst to give an epoxyether, but other attempts to prepare an epoxyether from an α-hydroxyketal have been fruitless; *cf.* THIS JOURNAL, **80**, 2276 (1958).

[8] F. Straus and H. Heinze, *Ann.*, **493**, 191 (1932).