hydrogen bromide per mole under conditions of the analytical method.[6]

Methylation of Acidic Material in Tubes 0-2, Countercurrent Distribution.—The material obtained in tubes 0–2 of the countercurrent distribution was a semi-solid. Its infrared spectrum was similar to that of methyl dimorphecolate (I), except that it had the characteristics of an acid rather than an ester. A 3.4-g. portion of this acidic material was dissolved in dry ether and added dropwise to a solution of 0.63 g. of diazomethane in 75 ml. of ether at room temperature. The excess diazomethane was removed by warming gently; on evaporation of solvent, an oily substance was obtained whose infrared spectrum was that of I.

Acknowledgments.—The authors are greatly indebted to Prof. Einar Stenhagen, Uppsala University, Uppsala, Sweden, and to Prof. Sune Bergström, Karolinska Institutet, Stockholm 60, Sweden, for correlating the infrared spectra of compounds V and VI with their synthetic materials. They also wish to thank Miss Janina Nowakowska of this Laboratory for gas chromatographic analysis of III; Mr. Henry Zobel for X-ray diffraction analysis of the 2,4-dinitrophenylhydrazone of VIII; Mr. C. R. Scholfield for valuable discussions of countercurrent distribution methods; Mr. Curtis Glass for infrared spectra; Mr. C. H. Van Etten for microanalyses; and Dr. Quentin Jones, Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture, for providing generous quantities of *Dimorphotheca* seed.

PEORIA, ILL.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND BACTERIOLOGY, STATE UNIVERSITY OF IOWA]

The Preparation and Properties of Some Oxidation Products of 1,11-Dodecadiene and 1,17-Octadecadiene[1]

BY S. WAWZONEK, P. D. KLIMSTRA,[2,3] R. E. KALLIO AND J. E. STEWART[3]

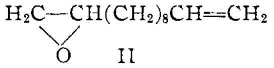
RECEIVED JULY 13, 1959

1,11-Dodecadiene, 1,2-epoxy-11-dodecene, 1,2,11,12-diepoxydodecane, 1,2,11,12-tetrahydroxydodecane, 1,17-octadecadiene, 1,2,17,18-diepoxyoctadecane and 1,2,17,18-tetrahydroxyoctadecane have been prepared for testing as possible intermediates in the oxidation of dodecane and octadecane by microörganisms. The epoxidation of both olefins with perbenzoic acid proceeded stepwise. The reaction of 1,2,11,12-diepoxydodecane with sodium *p*-bromophenoxide gave 1,2-epoxy-11-hydroxy-12-*p*-bromophenoxydodecane and bis-1,12-*p*-bromophenoxy-2,11-dihydroxydodecane. Tests with yeast *Candida lipolytica* indicate that the various derivatives of dodecane are oxidized more slowly than oxidation products involving one end of the hydrocarbon.

In the study of the oxidation of saturated hydrocarbons by certain microörganisms, oxidation products involving both ends of the hydrocarbons were required for the elucidation of the path of the oxidation. Work in this study was limited to the oxidation products of dodecane and octadecane and included the preparation of 1,11-dodecadiene (Ia), 1,17-octadecadiene (Ib), 1,2-epoxy-11-dodecene (II), 1,2,11,12-diepoxydodecane (IIIa), 1,2,17,18-diepoxyoctadecane (IIIb), 1,2,11,12-tetrahydroxydodecane (IVa) and 1,2,17,18-tetrahydroxyoctadecane (IVb).

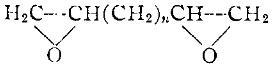
$H_2C{=}CH(CH_2)_nCH{=}CH_2$

Ia, $n = 8$
b, $n = 14$



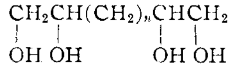
$\underset{O}{\underbrace{H_2C-CH}}(CH_2)_8CH{=}CH_2$

II



$\underset{O}{\underbrace{H_2C-CH}}(CH_2)_n\underset{O}{\underbrace{CH-CH_2}}$

IIIa, $n = 8$
b, $n = 14$



$\underset{OH}{CH_2}\underset{OH}{CH}(CH_2)_n\underset{OH}{CH}\underset{OH}{CH_2}$

IVa, $n = 8$
b, $n = 14$

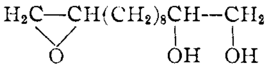
Both dienes were obtained from the action of allyl chloride on the Grignard reagent from 1,6-dichlorohexane.[4] Purification of the dienes was accomplished through the formation of the silver nitrate complexes and was necessary for 1,11-dodecadiene since this compound co-distilled with 1,6-dichlorohexane.

The preparation of 1,2,11,12-diepoxydodecane (IIIa) from the bis-chlorohydrin was not successful. The bis compound, which was not obtained pure, was resistant to cyclization with cold alkali.

Direct epoxidation of 1,11-dodecadiene (Ia) with peracetic acid gave 1,2,11,12-diepoxydodecane (IIIa). Better yields and less side products were obtained, however, using perbenzoic acid. The epoxidation at low temperatures was found to proceed stepwise with both reagents. Using an excess of perbenzoic acid one mole of the reagent added at 5–6° in less than two hours while the second mole required about ten hours to react (see Fig. 1).

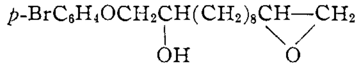
A similar stepwise addition of perbenzoic acid occurred with 1,17-octadecadiene (Ib) and 1,5-hexadiene and is shown in Fig. 1.

By interrupting the reaction with peracetic acid and 1,11-dodecadiene before it had gone to completion it was possible to isolate both the monoepoxide II and diepoxide IIIa together with a fraction which had the composition expected for 1,2-epoxy-11,12-dihydroxydodecane (V).



$\underset{O}{\underbrace{H_2C-CH}}(CH_2)_8\underset{OH}{CH}-\underset{OH}{CH_2}$

V



$p\text{-}BrC_6H_4OCH_2\underset{OH}{CH}(CH_2)_8\underset{O}{\underbrace{CH-CH_2}}$

VI

To determine whether this stepwise addition was characteristic of other reagents, the addition of bromine was studied with both 1,11-dodecadiene (Ia) and 1,17-octadecadiene (Ib) and found to be

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(1) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donor of said fund.

(2) Abstracted in part from the M.S. thesis, February, 1957, and the Ph.D. thesis, June, 1959, of P. D. Klimstra.

(3) American Chemical Society Petroleum Research Fund Predoctoral Fellows.

(4) F. Drahowzal, *Monatsh.*, **82**, 793 (1951).

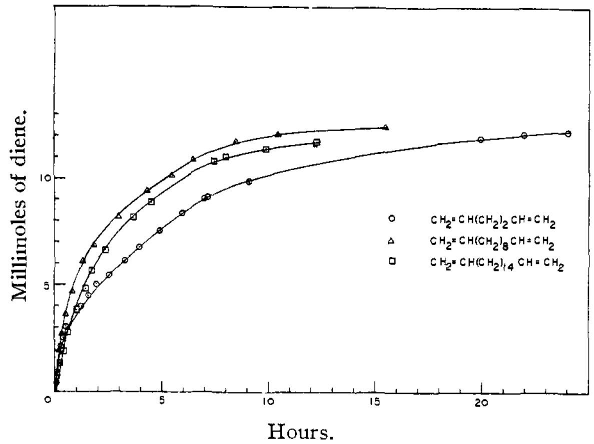
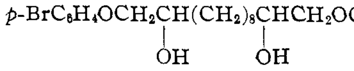


Fig. 1.—Rate of epoxidation of a, ω-dienes with perbenzoic acid using 12 millimoles of diene and 70 millimoles of acid.

too rapid to follow under the same conditions. The final product in each example was the tetrabromide.

In the formation of a derivative of 1,2,11,12-diepoxydodecane (IIIa) with sodium *p*-bromophenoxide, stepwise addition was likewise found to occur. The use of a more than twofold excess of sodium *p*-bromophenoxide gave after 48 hours of refluxing in benzene, 1,2-epoxy-11-hydroxy-12-*p*-bromophenoxydodecane (VI), unchanged diepoxide IIIa and the bis-1,12-*p*-bromophenoxy-2,11-dihydroxydodecane (VII). By using a ninefold excess



$$p\text{-}BrC_6H_4OCH_2\underset{OH}{CH}(CH_2)_8\underset{OH}{C}HCH_2OC_6H_4Br\text{-}p \qquad \text{VII}$$

of sodium *p*-bromophenoxide it was possible to obtain solely a mixture of the two *p*-bromophenoxy compounds (VI, VII).

The monoepoxide VI could be separated into two racemic modifications by fractional crystallization from hexane. The bis compound VII which can have *dl*- and *meso*-forms was obtained only in one form. Resolution of the monoepoxide VI through the phthalate was not successful since the salts with brucine and *l*-α-phenylethylamine were not crystalline.

The structures of the epoxide VI and the bis compound VII are based on their formation in basic medium. Epoxides under these conditions open at the primary carbon atom.[5]

The two isomeric epoxides VI gave identical infrared spectra and different X-ray diffraction diagrams. Polymorphic forms which would behave similarly were eliminated by the observation that mixtures of the two compounds melt at temperatures lower than those of the individual compounds. In polymorphism one form would be expected to be metastable and should change into the more stable form.

The possibility of isomeric products arises if the ring opening is not exclusively unidirectional and was excluded on the basis of the infrared spectra and the fact that only one bis compound (VII) was obtained.

Acid hydrolysis of 1,2,11,12-diepoxydodecane (IIIa) and 1,2,17,18-diepoxyoctadecane (IIIb) gave 1,2,11,12-tetrahydroxydodecane (IVa) and 1,2,-17,18-tetrahydroxyoctadecane (IVb). Only one isomer was isolated in each case.

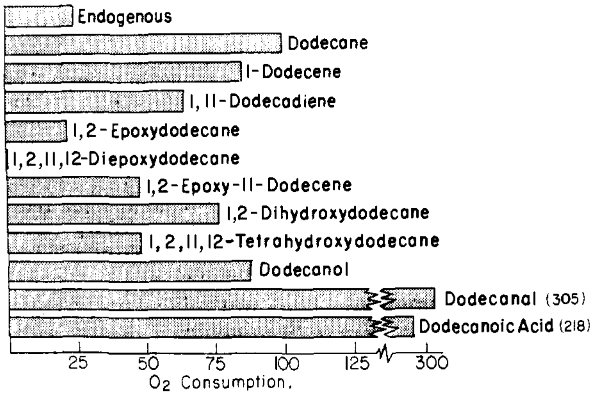


Fig. 2.—Oxidation of dodecane and various derivatives by the yeast *C. lipolytica.*

The yeast, *Candida lipolytica*, utilizes paraffins and olefins as a sole carbon source. Resting cells of *C. lipolytica* readily oxidize dodecane, 1-dodecene, dodecanol, dodecanal and dodecanoic acid. The "two ended" compounds 1,11-dodecadiene and 1,2,11,12-tetrahydroxydodecane were oxidized by dodecane grown cells of *C. lipolytica* but at a slower rate than the corresponding monofuctional compounds. 1,2-Epoxydodecane and 1,2,11,12-diepoxydodecane were toxic to the cells, particularly the latter which even inhibited endogenous respiration (Fig. 2). It was concluded that the two ended compounds tested were not intermediates in the oxidation of paraffins by *C. lipolytica*. Subsequent data derived from bacterial systems[6] indicated that biological oxidation of paraffins occurred at one terminal carbon and did not involve the formation of olefin, epoxide or 1,2-glycol.

In view of the behavior of the derivatives of dodecane a similar oxidation of 1,17-octadecadiene and its derivatives was not studied.

Experimental[7]

1,11-Dodecadiene (Ia).—To a saturated solution of silver nitrate (150 g.) in water (90 ml.) impure 1,11-dodecadiene[4] (62 g.) was added with vigorous stirring. The resulting solid mass was filtered, washed with cold absolute ethanol, and air-dried. Recrystallization twice from absolute ethanol gave a white solid which started to decompose at 50°.

Anal. Calcd. for $C_{12}H_{22}\cdot 2AgNO_3$: C, 28.47; H, 4.38. Found: C, 28.20; H, 4.41.

The solid complex was decomposed with water and the aqueous layer was extracted with ether. Removal of the ether gave a liquid which distilled at 83.5° (10 mm.), $n^{25}D$ 1.4413. The yield was 18.9% based on the 1,6-dichlorohexane used. A gas chromatogram using a silicone oil column at 175° gave only one peak. The literature[4] reports values of b.p. 80.7–81.2° (9 mm.) and $n^{20}D$ 1.4401.

1,17-Octadecadiene (Ib) was purified through its silver nitrate complex and distilled at 163–165° (10.5 mm.), $n^{25}D$ 1.4588. The yield was 12.6% based on the 1,6-dichlorohexane used in the Grignard reaction. The literature[8] reports values of b.p. 167–170° (10 mm.) and $n^{20}D$ 1.4515.

Reaction of Hypochlorous Acid with 1,11-Dodecadiene (Ia).—1,11-Dodecadiene (5 g.) in chloroform (30 ml.) was

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[5] H. C. Chitwood and B. T. Freure, This Journal, **68**, 680 (1946).

[6] J. E. Stewart, R. E. Kallio, D. P. Stevenson, A. C. Jones and D. O. Schissler, *J. Bacteriol.*, **78**, 441 (1959).

[7] Melting points and boiling points are not corrected.

[8] A. D. Petrov and M. A. Chel'tsova, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 267 (1940); *Chem. Abstr.*, **35**, 4730 (1941).

treated stepwise with a freshly prepared solution of hypochlorous acid[9] at 15–20°. The addition required 6 hours. The non-aqueous layer after purification gave a fraction which distilled at 155–161° (1 mm.), $n^{25}\text{D}$ 1.4890, $d^{25}\text{D}$ 1.115, yield 6.5 g. Infrared analysis indicated the absence of a carbon–carbon double bond.

Anal. Calcd. for $C_{12}H_{24}O_2Cl_2$: C, 53.12; H, 8.89. Found: C, 51.16; H, 7.79.

This fraction, when stirred with 20% sodium hydroxide for several hours, was obtained back essentially unchanged; $n^{25}\text{D}$ 1.4870.

1,2,11,12-Diepoxydodecane (IIIa).—1,11-Dodecadiene (Ia) (24 g.) was added to a chloroform (600 ml.) solution of perbenzoic acid (45 g.) and the resulting solution was allowed to stand at 5° for 24 hours. The chloroform solution after washing with 10% sodium hydroxide and water gave a liquid which distilled at 134–136° (5–6 mm.), $n^{20}\text{D}$ 1.4525, $d^{20}{}_4$ 0.919, yield 27 g. This compound gave a band at 1255 cm.$^{-1}$ for the epoxy group in the infrared region. No bands were visible at 1650 cm.$^{-1}$ for the double bond or 3400 cm.$^{-1}$ for a hydroxyl group.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.66; H, 11.18; epoxy, 16.16. Found: C, 72.30; H, 11.42; epoxy, 15.40.

1,2,17,18-Diepoxyoctadecane (IIIb).—1,17-Octadecadiene (Ib) (10 g.) when treated with perbenzoic acid (14 g.) in chloroform (200 ml.) by the method used for 1,11-dodecadiene (Ia) gave a white solid. Recrystallization from absolute ethanol gave 10.3 g. of material melting at 46–48.5°.

Anal. Calcd. for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13. Found: C, 76.20; H, 11.98.

1,2-Epoxy-11-dodecene (II).—1,11-Dodecadiene (Ia, 15 g.) was treated with 20% peracetic acid (95 g.) for 3 hours at 25–27°. The resulting solution was poured into water and extracted with ether. The ether after washing with sodium bicarbonate and water gave a colorless liquid which was fractionally distilled. A fraction (4.2 g.) boiling at 85° (8 mm.) had the composition expected for 1,2-epoxy-11-dodecene (II), $n^{30}\text{D}$ 1.4430, $d^{25}{}_4$ 0.815. This sample decolorized bromine in carbon tetrachloride.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.05; H, 12.16. Found: C, 78.91; H, 11.58.

The second fraction, boiling at 130–132° (4 mm.), gave 1.4 g. of the 1,2,11,12-diepoxydodecane (IIIa). Occasionally in this reaction a third fraction was obtained which boiled at 118–120° (4 mm.) and had the composition expected for 1,2-epoxy-11,12-dihydroxydodecane (V), $n^{30}\text{D}$ 1.4473. This sample gave a positive test with periodic acid.

Anal. Calcd. for $C_{12}H_{24}O_3$: C, 66.62; H, 11.14. Found: C, 66.62; H, 10.39.

1,2,11,12-Tetrabromodedecane.—To a mixture of chloroform (355 ml.) and dry benzene (36 ml.) containing bromine (17.8 g.) at 5°, 1,11-dodecadiene (Ia) (4.0 g.) in chloroform (10 ml.) was added. The bromine titer remained constant after 5 minutes and corresponded to the uptake of two moles of bromine. Excess bromine was removed with sodium bisulfite and the solvent was removed. Distillation at 170° (0.04 mm.) gave a liquid which corresponded in composition to the tetrabromide, $n^{20}\text{D}$ 1.5419, $d^{25}{}_4$ 1.790. The infrared spectra had no band at 1650 cm.$^{-1}$ which is shown by 1,11-dodecadiene.

Anal. Calcd. for $C_{12}H_{22}Br_4$: C, 29.65; H, 4.56. Found: C, 30.21; H, 4.60.

1,2,17,18-Tetrabromoöctadecane.—1,17-Octadecadiene (Ib) when treated with bromine in the same manner as 1,11-dodecadiene gave a solid which after one recrystallization from petroleum ether (30–60°) melted at 15–18°.

Anal. Calcd. for $C_{18}H_{34}Br_4$: C, 37.92; H, 6.02. Found: C, 37.77; H, 5.87.

1,2-Epoxy-11-hydroxy-12-*p*-bromophenoxydodecane (VI).—To a suspension of sodium *p*-bromophenoxide prepared from 2.0 g. of sodium and 21 g. of *p*-bromophenol in benzene (500 ml.) 1,2,11,12-diepoxydodecane (IIIa) (12 g.) was added and the mixture was refluxed with stirring for 48 hours. The resulting mixture was poured into water and the organic layer was washed with 10% sodium hydroxide. Removal of the benzene gave a solid which was taken up in hot hexane. Cooling gave a white solid (5.0 g.) melting at 57–69°.

Fractional crystallization several times from hexane gave two fractions melting at 76–77.5° and 65–67°, respectively. These purified fractions corresponded to 22.4 and 13.8%, respectively, of the original mixture.

Anal. Calcd. for $C_{18}H_{27}O_3Br$: C, 58.22; H, 7.32; epoxy, 4.31. Found (65–67°): C, 58.45; H, 7.30; epoxy, 4.20. Found (75–76°): C, 58.44; H, 7.40; epoxy, 4.24.

The two isomers gave identical infrared spectra. The band for the epoxy group at 1255 cm.$^{-1}$, however, was masked by the C–O stretching absorption. The spectra in fact were quite similar to those of the bis compound VII.

X-Ray diffraction diagrams obtained for these two isomers were different and pointed to *dl* modifications.

Evaporation of the first hexane filtrate followed by distillation gave 5 g. of unreacted 1,2,11,12-diepoxydodecane (IIIa). The residue in the distillation flask after recrystallization from absolute ethanol melted at 131–133° and analyzed for 1,12-bis-(*p*-bromophenoxy)-2,11-dihydroxydodecane (VII), yield 1 g.

Anal. Calcd. for $C_{24}H_{32}O_4Br_2$: C, 52.95; H, 5.93. Found: C, 52.55; H, 5.95.

Refluxing the diepoxide IIIa (2 g.) with a greater excess of sodium *p*-bromophenoxide (15 g. of *p*-bromophenol and 0.3 g. of sodium) for 48 hours gave only the mono-*p*-bromophenoxy (VI) (0.72 g.) and the bis-*p*-bromophenoxy (VII) (0.34 g.) compounds.

Reaction of 1,2-Epoxy-11-hydroxy-12-*p*-bromophenoxydodecane (VI) **with Phthalic Anhydride.**—A mixture of 1.2 g. of the 74–75° melting isomer was heated with phthalic anhydride (10 g.) for 125 hours at 120–125°. After 30 hours, 4 ml. of dry toluene was added to wash down the sublimed phthalic anhydride. The resulting mixture upon cooling was added to water (750 ml.) containing sodium carbonate (12.5 g.). The solid gradually dissolved after 24 hours of stirring and the resulting solution was decolorized twice with charcoal. Partial acidification of the colorless solution gave a tan solid melting at 64–67°, yield 0.6 g.

Anal. Calcd. for $C_{26}H_{31}O_6Br$: C, 60.1; H, 6.01; neut. equiv., 519. Found: C, 59.64; H, 6.07; neut. equiv., 525.

The residue from the neutralization equivalent determination after acidification proved to be the unchanged phthalate.

No crystalline material was obtained when the phthalate was treated with brucine in either acetone or a mixture of methanol and chloroform or with *l*-α-phenylethylamine in methanol, chloroform, and acetone.

1,2,11,12-Tetrahydroxydodecane (IVa).—1,2,11,12-Diepoxydodecane (IIIa, 2.0 g.) was refluxed in dioxane (135 ml.) with 45 ml. of 2 *M* sulfuric acid for 24 hours and allowed to stand for an additional 24 hours at room temperature. The mixture was extracted with ether and the resulting aqueous acidic layer was neutralized with sodium bicarbonate. The precipitate obtained proved to be the tetrahydroxy compound IVa. More of this compound was obtained from the ether extract; total yield, 1.32 g. Several recrystallizations from water gave a solid melting at 112.5–114°.

Anal. Calcd. for $C_{12}H_{26}O_4$: C, 61.51; H, 11.18. Found: C, 62.03; H, 11.22.

1,2,17,18-Tetrahydroxyoctadecane (IVb) was prepared in a similar manner to that used for the dodecane derivative and was obtained in a 94.6% yield. After one recrystallization from absolute ethanol the solid melted at 132–134°.

Anal. Calcd. for $C_{18}H_{38}O_4$: C, 67.87; H, 12.02. Found: C 67.54; H, 11.44.

1,2-Dihydroxydodecane was prepared from 1-dodecene by the method of Swern, Billen and Scanlon.[10]

Materials.—Dodecane and 1-dodecene were obtained from The American Petroleum Institute Standards; 1,2-epoxydodecane from the Buffalo Electrochemical Co.; dodecanol-1, dodecanoic acid from Matheson, Coleman and Bell; and dodecanal from the research division of Armour and Co.

Rate Studies with Perbenzoic Acid.—To a solution of chloroform (300 ml.) and benzene (30 ml.) containing per-

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[9] G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 158.

[10] D. Swern, G. N. Billen and J. T. Scanlon, THIS JOURNAL, **68**, 1504 (1946).

benzoic acid (9.64 g., 0.07 mole) at 5°, 0.012 mole of diene in chloroform (2 ml.) was added and the solution was well mixed. Periodically the amount of perbenzoic acid present was determined iodometrically. The results obtained are shown in Fig. 1.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Some Syntheses and Structures in the 9,10-Dihydro-9,10-ethanoanthracene Series. I[1a]

BY EUGENE I. SNYDER[1b] AND ROBERT A. CLEMENT[1c]

RECEIVED SEPTEMBER 2, 1959

Syntheses of 11-keto-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene, its *p*-toluenesulfonate ester and 11-keto-12-methylene-9,10-dihydro-9,10-ethanoanthracene are described. Rigorous structure proofs for these compounds and the precursors are presented.

Introduction

For a projected study of the course of nucleophilic displacement upon a ketone substituted in the β-position with a leaving group, we required a β-tosyloxy ketone and the corresponding β-ketol and α,β-unsaturated ketone with certain necessary structural and desirable physical features. The 9,10 - dihydro - 9,10 - ethanoanthracene system appeared to be the simplest system which incorporated these features, and we set out to synthesize 11 - keto - 12 - hydroxymethyl - 9,10 - dihydro - 9,10-ethanoanthracene (VI), its *p*-toluenesulfonate ester VIII and 11-keto-12-methylene-9,10-dihydro-9,10-ethanoanthracene (IX).

One of our early attempts to synthesize these compounds proceeded from 11-bromo-*trans*-12-carboxy-9,10-dihydro-9,10-ethanoanthracene (XI) as an intermediate. This compound had been carried through several steps in a synthesis when it became apparent that there had occurred rearrangement of the 9,10-dihydro-9,10-ethanoanthracene skeleton at some stage in the sequence. Simultaneously, there appeared a paper by Vaughan[2] in which this stage was identified as the initial hydrolysis step and the product obtained therein as *exo* - 2 - hydroxy - *anti* - 8 - carboxydibenzo[c.f]bicyclo[3.2.1]octane (X). We then turned our attention to procedures which did not involve compounds with leaving groups on the ethano bridge and which, consequently, would likely avoid the difficulty of skeletal rearrangement.

In this paper we report our best synthetic procedures to the desired compounds VI, VIII and IX, and structure proofs for them and for their precursors.

Results

The syntheses of the desired compounds proceeded from 11-keto-9,10-dihydro-9,10-ethanoanthracene[3] (I) and are outlined in Fig. 1. The ketone was transformed, by successive treatment with sodium triphenylmethide and carbon dioxide, to 11-keto-12-carboxy-9,10-dihydro-9,10-ethanoanthracene (II) which was converted to its methyl ester III for purification. Ketalization of III yielded 11,11-dimethoxy-12-carbomethoxy-9,10-dihydro-9,10-ethanoanthracene (IV) which was converted to 11,11-dimethoxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene (V) by reduction with lithium aluminum hydride. *trans*-Ketalization of V with acetone afforded the desired β-ketol VI. Treatment of V with *p*-toluenesulfonyl chloride in pyridine gave 11,11-dimethoxy-12-tosyloxymethyl - 9,10 - dihydro - 9,10 - ethanoanthracene (VII) which, upon *trans*-ketalization with acetone, afforded the desired β-tosyloxy ketone VIII. The desired α,β-unsaturated ketone IX was obtained in excellent yield by the rapid reaction of VIII with a molar equivalent of sodium hydroxide in aqueous dioxane at room temperature. Overall yields, based on ketone I, were: of VI, 30%; of VIII, 29%; of IX, 25%.

Explicit structure proofs for our 9,10-dihydro-9,10-ethanoanthracenes were required in view of the rearrangements which have been noted in this system,[2,4,5] and in view of our experience with these rearrangements (see Introduction), they were conducted contemporarily with the synthesis procedures.

The structure of the keto acid II was established by its decarboxylation, at its melting point, to the ketone I. There seemed little probability of rearrangement in the formation of the keto ester III, but the structure of the ketal ester IV was less certain since its formation required, at least formally, a positive charge on the ethano bridge. However, the ketal ester, on *trans*-ketalization with acetone, regenerated the keto ester III, demonstrating identity of carbon skeletons. There seemed little chance for rearrangement in the reduction of IV to the ketal alcohol V so that we were reasonably confident of the structures through that of V.

The structures II through V were confirmed, and the identity of the ketol VI, was established by the reduction of VI in glacial acetic acid by the Clemmensen procedure to the known[6] acetate XV of 11-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene (XIV). The alcohol was formed[6] in a Diels–

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[1] (a) Abstracted from a portion of the Ph.D. Dissertation of Eugene I. Snyder, Dept. of Chemistry, University of Chicago, 1959; (b) National Science Foundation Predoctoral Fellow, 1956–1959; (c) to whom inquiries should be addressed.

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