dropwise with stirring under nitrogen to 0.56 g. (0.0806 g.-atom) of finely-cut lithium strips. The mixture was stirred 0.5 hr. after there was no observable change, the lithium reagent then being filtered through glass wool into another dry flask under nitrogen. Then a solution of 5.3 g. (0.0156 mole) of ethyl 3,3-bis(*p*-dimethylaminophenyl)propionate in 100 ml. of ether was added to the stirred lithium aryl solution. Two hours after addition the reaction was poured into a saturated ammonium chloride solution. The ether layer was separated and the water layer extracted with chloroform. The combined organic layers were evaporated *in vacuo* and the residue recrystallized from acetone to give the carbinol, m.p. 187–187.5°, in a yield of 4.3 g. (0.008 mole), 51%.

Anal. Calcd. for $C_{35}H_{44}N_4O$: C, 78.32; H, 8.26; N, 10.44. Found: C, 77.98; H, 8.15; N, 10.16.

Preparation of 1,1,3,3-tetrakis(p-dimethylaminophenyl)propane (XI). The propanol X, 2.0 g. (0.00373 mole), was dissolved by heating to boiling in 150 ml. of absolute ethanol, cooled, and reduced in the presence of 1 g. of 5% palladium on charcoal under a pressure of 40 pounds of hydrogen at 40–50°. After 2 hr. there was no further absorption of hydrogen. The cooled solution was filtered and evaporated to dryness *in vacuo* to yield a sticky semisolid. It was recrystallized repeatedly from ethanol, m.p. 180–181°, with prior softening. The yield was low.

Anal. Calcd. for $C_{35}H_{44}N_4$: C, 80.72; H, 8.52; N, 10.76. Found: C, 80.59; H, 8.63; N, 10.87.

Preparation of 2,2,4,4-tetrakis(p-dimethylaminophenyl)pentane. An attempt was made to prepare this compound according to the method of von Braun.[9] A Carius tube was charged with 10 g. (0.1 mole) of acetylacetone, 48.4 g. (0.4 mole) of dimethylaniline and 33.4 ml. of concd. hydrochloric acid, sealed, and heated to 150° for 6 hr. The cooled tube was opened and the viscous contents inverted into an excess of 10% aqueous sodium bicarbonate. The product was extracted with ether, the ether removed, and the residue steam-distilled. The yellow liquid in the distillation flask solidified on cooling; it was extracted with ether, the ether evaporated, and the residue recrystallized from ethanol-water, m.p. 82–83.5°. Although its infrared spectrum was almost identical with that of VII, a molecular weight determination (ebullioscopic in ethanol) established that the product was 2,2-bis(*p*-dimethylaminophenyl)propane, m.m.p. with authentic sample, 81–83°.

Anal. Calcd. for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92; mol. wt., 282. Found: C, 81.03; H, 9.17; N, 9.96; mol. wt., 256.

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INDIANAPOLIS, IND.

[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. II[1a]

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

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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, proceeding through the *cis*- and *trans*-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracenes as intermediates.

In a previous publication[2] we reported synthetic procedures for the preparation of 11-keto-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene (III), 11-keto-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene (VII), and 11-keto-12-methylene-9,10-dihydro-9,10-ethanoanthracene (IV), along with rigorous structure proofs for these compounds. In this paper we present alternative syntheses of III, VII, and IV which involve different procedures but which are less satisfactory in terms of yields and convenience. The structures concerned are collected in Fig. 1.

RESULTS

Starting material for these transformations was 11-keto-12-carbomethoxy-9,10-dihydro-9,10-ethanoanthracene (I)[2] which was reduced with lithium aluminum hydride to a mixture of the *cis*- and *trans*-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracenes (II). Treatment of this isomeric mixture with acetone and cupric sulfate effected a clean separation of the racemates, the *cis* diol (IIa) being converted to *cis*-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene isopropylidene ketal (V). *trans* Diol (IIb) was recovered from the reaction mixture and *cis* diol (IIa) was obtained by subsequent hydrolysis of the ketal (V). Assignment of configurations to the diols (II) was made on the basis of this selective formation of isopropylidene ketal.

The ketol (III) was conveniently prepared by selective oxidation of the secondary hydroxyl functions in the diol mixture (II) with *N*-bromo-

(1) (a) Abstracted from a portion of the Ph.D. dissertation of Eugene I. Snyder, Department of Chemistry, University of Chicago, 1959. (b) National Science Foundation Fellow, 1956–59. (c) Author to whom inquiries should be addressed.

(2) E. I. Snyder and R. A. Clement, *J. Am. Chem. Soc.*, **82**, 1424 (1960).

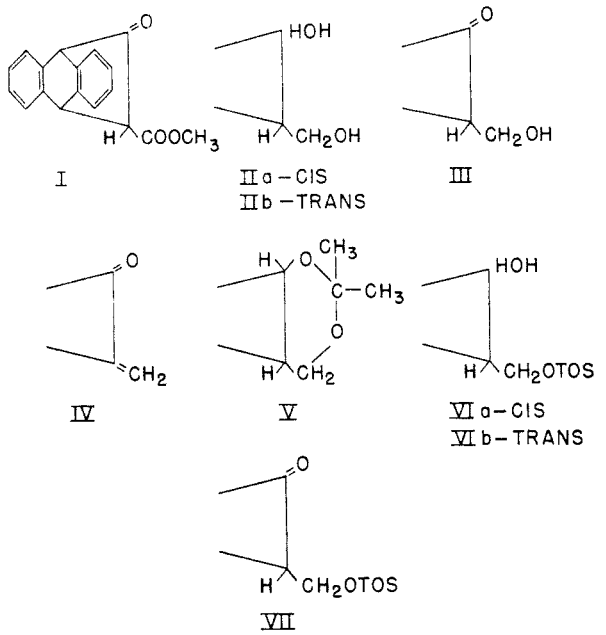

Fig. 1. Some substituted 9,10-dihydro-9,10-ethanoanthracenes. All structures have the 9,10-dihydro-9,10-ethanoanthracene skeleton

acetamide.[3] In an attempt to prepare the keto tosylate (VII), the ketol (III) was treated with tosyl chloride in pyridine. However, the only identifiable product, obtained in poor yield, proved to be the methylene ketone (IV). Presumably, the keto tosylate (VII) was formed but was converted to the methylene ketone (IV) by a subsequent elimination reaction.

The keto tosylate (VII) was successfully prepared, and in comparable yields, by separate oxidations with *t*-butyl hypochlorite[4] of the *cis*- and *trans* - 11 - hydroxy - 12 - tosyloxymethyl-9,10 - dihydro - 9,10 - ethanoanthracenes (VIa and VIb). These latter were prepared from the *cis*- and *trans* diols, IIa and IIb, respectively, by selective tosylations of the primary hydroxyl functions. The separate conversions of the diols IIa and IIb to the common keto tosylate (VII) confirmed their identities as *cis-trans* isomers.

The procedures reported here, although they yielded the desired compounds III, VII, and IV, are inferior to those reported earlier.[2]

EXPERIMENTAL[5]

Reduction of 11-keto-12-carbomethoxy-9,10-dihydro-9,10-ethanoanthracene (I). The keto ester (I)[2] (2.8 g., m.p. 139°) was placed in the thimble of a continuous-return Soxhlet extractor and extracted into a slurry of lithium aluminum hydride (2.0 g.) in boiling ether (300 ml.). After all the keto ester had been extracted from the thimble, the reaction mixture was treated with methanol and then with 10% aqueous sulfuric acid. The aqueous layer was separated, extracted with ether, and the combined ether extracts were dried over magnesium sulfate. After filtration, removal of ether at reduced pressure afforded an oil (2.2 g., 87%) which solidified on being triturated with benzene. This solid, a mixture of the *cis*- and *trans* diols (IIa and IIb), melted over a range, generally 125–135°, and was used directly in subsequent manipulations.

Separation of cis- and trans-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracenes (IIa and IIb). *cis-11-Hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene isopropylidene ketal* (V). The mixture of diols (IIa and IIb) (1.25 g., as obtained directly from reduction) was dissolved in reagent-grade acetone (30 ml.) and stirred at room temperature with cupric sulfate (1.3 g.) for 39 hr. At the end of this time the mixture was filtered and the oil obtained by removal of solvent was dissolved in benzene (5 ml.). After 24 hr., the solid which had appeared was isolated by filtration, the benzene filtrate being preserved for isolation of the ketal (see below). This solid (0.457 g., 36% on diol mixture) was good-quality *trans* diol (IIb), m.p. 151–153°. Two recrystallizations from ethyl acetate afforded *trans-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene* (IIb), m.p. 154.1–154.9°. In the infrared (potassium bromide pellet) IIb exhibited absorption at 3300 cm.$^{-1}$ (hydroxyl), and, among others, at 1045 cm.$^{-1}$

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.94; H, 6.39. Found: C, 80.98; H, 6.62.

The benzene filtrate obtained from isolation of *trans* diol (IIb) was evaporated to yield, after one recrystallization from methanol, good-quality ketal (V) (0.579 g., 40% on diol mixture), m.p. 146–147°. Several recrystallizations from methanol afforded *cis-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene isopropylidene ketal* (V), m.p. 148.0–148.1°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 81.93; H, 6.84.

The *cis* diol (IIa) was obtained from ketal (V) by ketal exchange. A solution of ketal (V) (0.140 g., m.p. 147°) in absolute methanol (11 ml.) was stirred at room temperature with cupric sulfate (0.14 g.) for 44 hr. Dilution with water, extraction with ether, and removal of the ether at reduced pressure afforded crude *cis* diol (IIa) (0.118 g., 97%), m.p. 141–145°. One recrystallization from benzene raised the m.p. to 149–150°. Additional crystallizations from benzene yielded *cis-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene* (IIa), m.p. 150.9–151.0°, m.p. 130–145° on admixture with *trans* diol (IIb). In the infrared (potassium bromide pellet) IIa exhibited a spectrum similar to that of IIb with absorption at 3320 cm.$^{-1}$ (hydroxyl), but lacking absorption at 1045 cm.$^{-1}$

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.94; H, 6.39. Found: C, 80.76; H, 6.34.

11-Keto-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene (III). A mixture of the diols IIa and IIb (0.830 g., as obtained directly from reduction) was dissolved in absolute methanol (8 ml.) and to the solution were added pyridine (0.8 ml.) and *N*-bromoacetamide (0.621 g.). The solution was kept at room temperature and in the dark for 68 hr., at the end of which time it was diluted with water and treated with sodium bisulfite to decompose the excess *N*-bromoacetamide. The resulting solution was extracted with ether and the ether extract was washed with dilute hydrochloric acid followed by water and dried over magnesium sulfate. Filtration, followed by removal of the solvent, yielded a yellow oil which was chromatographed on 64 g. of Florisil. Elution of the column with 1.5% ether in benzene yielded 0.392 g. (48%) of crude ketol (III) as an oil which solidified on being triturated with carbon tetrachloride to give good-quality ketol (III), m.p. 137.0–137.8°. This material was

(3) T. H. Kritchevsky, D. L. Garmaise, and T. F. Gallagher, *J. Am. Chem. Soc.*, **74**, 483 (1952); E. P. Olivetto, H. L. Herzog, and E. B. Hershberg, *J. Am. Chem. Soc.*, **75**, 1505 (1953); R. E. Jones and F. W. Kocher, *J. Am. Chem. Soc.*, **76**, 3682 (1954).

(4) C. A. Grob and H. J. Schmid, *Helv. Chim. Acta*, **36**, 1763 (1953).

(5) Melting points are corrected. We are indebted to Mr. William Saschek of this Department for the analyses.

identical with authentic[2] ketol (III) (m.p. 139.6–140.0°) by the criteria of mixture melting point and infrared spectra.

Attempted tosylation of 11 keto-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene (III). *11-Keto-12-methylene-9,10-dihydro-9,10-ethanoanthracene* (IV). A solution of crude ketol (III) (0.455 g., 1.82 mmoles) and *p*-toluenesulfonyl chloride (0.380 g., 1.99 mmoles) in dry pyridine (4 ml.) was kept at room temperature for 40 hr. The solution was then diluted with water, acidified, and extracted with ether.

From the ether extract after drying over magnesium sulfate, filtering, and removing ether, there was obtained an oil which was chromatographed on Florisil. The only identifiable material obtained from the chromatogram was 0.085 g. (20%) of crude methylene ketone (IV), which was eluted with benzene. This material, after one recrystallization from methanol, afforded methylene ketone (IV), m.p. 224.8–225.0°, which was identical with authentic[2] methylene ketone (IV) (m.p. 223.0–224.0°) by the criteria of mixture melting point and infrared spectra.

cis- and trans-11-Hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracenes (VIa *and* VIb). A solution of *cis* diol (IIa) (0.530 g., 2.10 mmoles) and *p*-toluenesulfonyl chloride (0.450 g., 2.36 mmoles) in a mixture of dry benzene (7 ml.) and dry pyridine (2 ml.) was kept at room temperature for 17 hr. The mixture was then diluted with water and extracted with ether, the ether extract being washed with dilute hydrochloric acid, then water, and finally being dried over magnesium sulfate. Filtration and removal of solvent yielded a glass which solidified on being triturated with carbon tetrachloride. Recrystallization of this solid from methanol gave 0.319 g. (37%) of the *cis*-hydroxy tosylate (VIa), m.p. 152°. An additional recrystallization from methanol afforded *cis-11-hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene* (VIa), m.p. 152.0–152.2°. In the infrared (chloroform solution) VIa exhibited absorption at 3540 and 3370 cm.$^{-1}$ (hydroxyl) and, among others, at 1365, 1192, and 1180 cm.$^{-1}$ (tosylate).

Anal. Calcd. for $C_{24}H_{22}O_4S$: C, 70.89, H, 5.46. Found: C, 70.72; H, 5.64.

For the preparation of *trans*-hydroxy tosylate (VIb), a solution of the *trans* diol (IIb) (0.177 g., 0.703 mmole) and *p*-toluenesulfonyl chloride (0.156 g., 0.817 mmole) in dry pyridine (6 ml.) was kept at room temperature for 41 hr. The reaction mixture was then processed as above to yield 0.243 g. of crude product which was chromatographed on Florisil. Elution of the column with 5% ether in benzene afforded 0.140 g. (49%) of *trans-11-hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene* (VIb) as a glass which could not be induced to crystallize. In the infrared (chloroform solution) this material exhibited absorption at 3540 cm.$^{-1}$ (hydroxyl) and, among others, at 1367, 1192, and 1178 cm.$^{-1}$ (tosylate); its spectrum was distinct from that of the *cis*-hydroxy tosylate (VIa) and indicated no contamination by VIa.

After elution of the *trans*-hydroxy tosylate (VIb) from the chromatographic column, there was obtained (with 3% methanol in benzene) 0.026 g. (34% recovery) of unchanged *trans* diol (IIb).

11-Keto-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene (VII). (A). *From cis-11-hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene* (VIa). A solution of *cis*-hydroxy tosylate (VIa) (0.199 g., m.p. 152°), *t*-butyl hypochlorite[6] (0.120 g.) and pyridine (0.139 g.) in chlorobenzene (4 ml.) was permitted to remain at room temperature for 9.5 hr. The solution was then diluted with ether, washed with aqueous sodium bisulfite, water, dilute hydrochloric acid, water, and then dried over magnesium sulfate. After filtration, solvent was removed under reduced pressure to yield the keto tosylate (VII) as a solid which, after one recrystallization from ethanol, melted at 149–150° dec., and amounted to 0.071 g. (36%). Two additional recrystallizations from ethanol afforded material, m.p. 151.0–151.8° dec., which was identical with authentic[2] keto tosylate (VII) (m.p. 152° dec., and 167° dec.) by the criteria of mixture melting point and infrared spectra.

(B). *From trans-11-hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene* (VIb). A solution of *trans*-hydroxy tosylate (VIb) (0.126 g., as obtained from chromatography), pyridine (0.100 g.), and *t*-butyl hypochlorite[6] (0.054 g.) in chlorobenzene (3 ml.) was permitted to remain at room temperature for 16 hr. Isolation procedures as in (A) yielded, after one recrystallization from ethanol, 0.040 g. (32%) of keto tosylate (VII), m.p. 152–153° dec. This material was identical with that obtained in (A) by the criteria of mixture melting point and infrared spectra.

CHICAGO 37, ILL.

(6) H. M. Teeter and E. W. Bell, *Org. Syntheses*, **32**, 20 (1952).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Chlorides Derived from 1-Ethynylcyclohexanol[1]

G. F. HENNION AND C. A. LYNCH, JR.[2]

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The action of thionyl chloride on 1-ethynylcyclohexanol (I), under a variety of conditions, invariably led to a complex mixture only partially separable by fractional distillation. The following products were identified: unchanged carbinol (I), 1-ethynylcyclohexyl chloride (II), 1-ethynylcyclohexene (III), 1-(α-chlorovinyl)cyclohexene (IV), cyclohexylidenevinyl chloride (V), and 1-(β-chlorovinyl)cyclohexene (VI). The *t*-chloride (II) was always formed in minor amounts only. Cyclohexylidenevinyl chloride (V) is sensitive to thermal and prototropic rearrangement to the isomer (VI) and could not be isolated in high purity. Independent syntheses produced the isomers, II, IV, and VI in satisfactory yield and purity.

Various studies underway in this laboratory require assorted higher *t*-acetylenic chlorides, RR′C(Cl)—C≡CH. Where R and R′ are small alkyl groups, the preparations are easily accomplished by reaction of *t*-acetylenic carbinols with concentrated hydrochloric acid.[3] As this method has not proved satisfactory where R and (or) R′ are large, other preparative methods have been sought. We wish to summarize now a de-

(1) Paper no. 72 on substituted acetylenes; previous paper by G. F. Hennion and R. S. Hanzel, *J. Am. Chem. Soc.*, (in press).

(2) Dow Chemical Company Fellow, 1957–58. Abstracted from the Ph.D. Dissertation of C. A. L., Jr.