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.

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[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]

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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. 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.

[2] W. R. Vaughan and A. C. Schoenthaler, THIS JOURNAL, **80**, 1956 (1958).

[3] S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

[4] W. R. Vaughan and K. M. Milton, THIS JOURNAL, **74**, 5623 (1952).

[5] W. R. Vaughan, M. V. Anderson, Jr., and R. Q. Little, Jr., *ibid.*, **76**, 1748 (1954); W. R. Vaughan and R. Q. Little, Jr., *ibid.*, **76**, 2952, 4130 (1954); W. R. Vaughan and A. C. Schoenthaler, *ibid.*, **79**, 5777 (1957).

[6] K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).

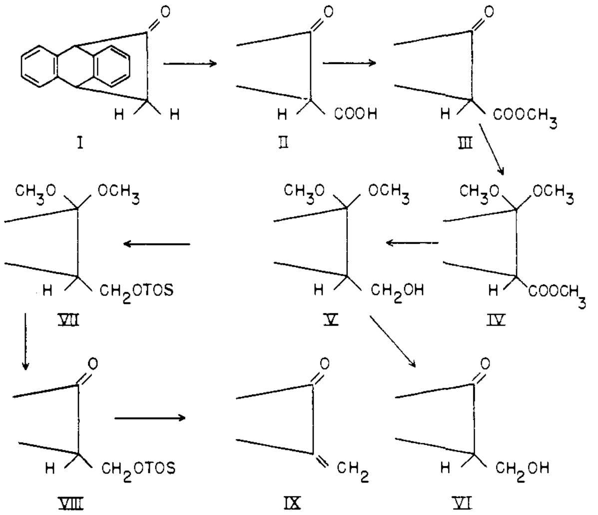

Fig. 1.—Synthetic routes for some 9,10-dihydro-9,10-ethanoanthracenes. All compounds have the 9,10-dihydroanthracene skeleton.

Alder reaction between allyl alcohol and anthracene, so the structures XIV and XV are certain. The Clemmensen reduction afforded, in addition to XV, a small yield of a hydrocarbon which we believe to be 11-methyl-9,10-dihydro-9,10-ethanoanthracene (XIII) on the basis of its empirical formula and its infrared spectrum.

We attempted to establish the structure of the ketal tosylate VII by converting it to the ketal of the known[4,7] 11-keto-12-methyl-9,10-dihydro-9,10-ethanoanthracene (XII) by reduction with lithium aluminum hydride, a procedure employed successfully by Walborsky[8] with similar compounds. With the ketal tosylate VII S–O cleavage occurred exclusively, and the only product isolated was the ketal alcohol V. However, since the structure of V was certain, the transformation of VII to V established the structure of VII.

The structure of the keto tosylate VIII was to have been proved by a Clemmensen reduction to the known alcohol XIV (or an ester thereof). However, the reduction took an unexpected, although not inexplicable, course, and the only crystalline product isolated was the methyl ketone XII. Although unexpected, the transformation of VIII to XII served as a structure proof for VIII. The structure of XII appeared to be firm, but we obtained supporting evidence from its nuclear magnetic resonance spectrum which possessed an absorption pattern precisely as required by the assigned structure.

The structure of the methylene ketone IX was established by catalytic hydrogenation to the methyl ketone XII.

For our projected study of the course of nucleophilic displacement upon a ketone substituted in the β-position with a leaving group, we desired a system in which the methylene ketone was a transitory intermediate in the conversion of the β-tosyloxy ketone to the β-ketol. In the present system, the methylene ketone is not a transitory intermediate, but the main product of the interaction of the β-tosyloxy ketone with hydroxide ion. Although inappropriate for our projected study, the present system is of considerable interest in another respect. The steric features of the keto tosylate VIII are such that the elimination reaction involved in its transformation to the methylene ketone IX is almost certainly a *cis* elimination. Thus, this reaction appears to be another example of a facile *cis* elimination promoted by the attachment of a strong electron-withdrawing group to the β-carbon atom, and is similar to those reactions studied by Bordwell and Pearson[9] where the electron-withdrawing group is sulfonyl. Since the acyl radical is more effective than the sulfonyl radical in promoting acidity, whether measured by rate or by equilibrium phenomena,[10] the present system appears to be a good one for observing an ElcB-type elimination. This possibility is under investigation.

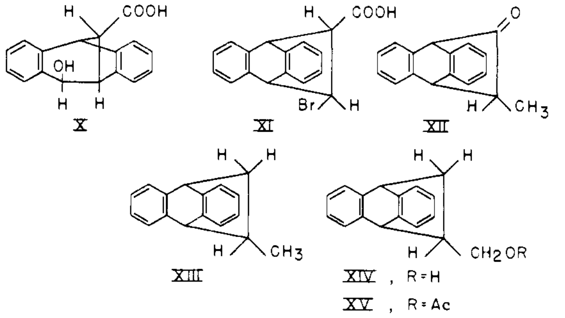

Fig. 2.—Additional structures in the 9,10-dihydro-9,10-ethanoanthracene series.

Experimental[11]

11-Keto-9,10-dihydro-9,10-ethanoanthracene (I).—The preparation was conducted essentially as described by Wawzonek[3] except that 11-hydroxy-9,10-dihydro-9,10-ethanoanthracene was prepared by hydrogenolysis of its acetate with lithium aluminum hydride. The ketone, m.p. 147–151° (lit.[3] m.p. 152.5–153.0°), of sufficient purity for subsequent operations was obtained in an over-all yield of 45% from anthracene.

11-Keto-12-carboxy-9,10-dihydro-9,10-ethanoanthracene (II).—The preparation of II was carried out in a 1-l., 3-necked flask equipped with a gas inlet tube which extended half way into the flask and a mercury-sealed gas outlet tube, the third neck being equipped to serve as an inlet both for nitrogen gas and the sodium triphenylmethide solution. All operations were performed under a nitrogen atmosphere, and stirring was by a magnetic stirring bar. To a stirred ethereal solution of the ketone I (15.2 g., m.p. 147–151°) was added sufficient ethereal sodium triphenylmethide solution[12] to produce a permanent red color. The flask was then cooled in a Dry Ice-bath, and when the temperature of the contents had been reduced to *ca.* −35°, a rapid stream of dry carbon dioxide was admitted through the gas inlet tube into the vigorously stirred solution. Solid formed immediately, and passage of the carbon dioxide was continued for 15 min. After the reaction mixture had warmed to room temperature, it was added to an approximately equal volume of water and extracted several times with 10% aqueous sodium carbonate. The aqueous extracts were back-extracted with ether and then carefully acidified with concd.

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(7) W. E. Noland, M. S. Baker and H. I. Freeman, THIS JOURNAL, **78**, 2233 (1956).

(8) H. M. Walborsky, *Helv. Chim. Acta*, **36**, 1251 (1953).

(9) See, for example, J. Weinstock, R. G. Pearson and F. G. Bordwell, THIS JOURNAL, **78**, 3473 (1956).

(10) R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2439 (1953).

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

(12) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

hydrochloric acid. After being refrigerated for 16 hr., the solution yielded 12.8 g. of the crude acid II, probably as its hydrate, which had m.p. 133° dec. after melting and evolving gas at about 125° and resolidifying. This material was esterified directly. The analytical sample was obtained from another preparation only after several recrystallizations from benzene and finally from methanol–water. It had m.p. 146.1–146.8° dec.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.37; H, 4.72.

An aqueous ethanolic solution of this sample gave a blue color with 1% ferric chloride solution. From a sample of II, held at its melting point until gas evolution was complete, was isolated material, m.p. 153.0–153.1°, which was identical with a purified sample of the ketone I by the criteria of mixture melting point and infrared spectra. An air dried sample of II, obtained from crude acid after several recrystallizations from benzene, had m.p. 143.5–144.0° dec. after melting at about 130° and resolidifying, and apparently contained benzene of crystallization.

Anal. Calcd. for $C_{17}H_{12}O_3.C_6H_6$: neut. equiv., 342. Found: neut. equiv., 337, 339.

11-Keto-12-carbomethoxy-9,10-dihydro-9,10-ethanoanthracene (III).—An ethereal solution of the crude keto acid II (12.8 g.), prepared as described above, was esterified with diazomethane[13] and the solution was refrigerated. After several hours, there had precipitated 6.46 g. of pure crystalline keto ester III, m.p. 139.0–139.5°. An additional 3.42 g. of pure III was obtained by concentration of the mother liquors to give a total of 9.88 g. (52% based on ketone I), m.p. 139.0–139.5°. The analytical sample was obtained as long rectangular prisms, m.p. 139.8–140.0°, by recrystallization from ethanol, and showed absorption in the infrared (KBr pellet) at 1740 (ester) and 1705 cm.$^{-1}$ (ketone). It gave no color with aqueous alcoholic ferric chloride.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.69; H, 5.07. Found: C, 77.57; H, 5.20.

11,11-Dimethoxy-12-carbomethoxy-9,10-dihydro-9,10-ethanoanthracene (IV).—A solution of the keto ester III (3.323 g., m.p. 139.0–139.5°), ethyl orthoformate (2.9 g.), absolute methanol (70 ml.), dry benzene (30 ml.) and *p*-toluenesulfonic acid monohydrate (0.8 g.) was held under reflux while distillate was removed continuously. After 6.5 hr., when 32 ml. of distillate had been collected, the cooled reaction mixture was added to 200 ml. of iced 1.5% aqueous sodium carbonate. The solid which formed was removed by filtration and digested with 150 ml. of methanol which had been made basic by the addition of a little aqueous ammonia. From this solution, after refrigeration, there was obtained 2.589 g. (67%) of the pure ketal ester IV, m.p. 185.0–186.0°. The analytical sample was prepared by two recrystallizations from methanol and was obtained as cubic crystals, m.p. 185.1–186.0°. In the infrared (KBr pellet) this material had a single absorption in the carbonyl region at 1720 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.04; H, 6.21. Found: C, 73.83; H, 5.97.

A small sample (0.209 g.) of IV was *trans*-ketalized by heating under reflux for 4.5 hr. in 9 ml. of acetone which contained 0.030 g. of *p*-toluenesulfonic acid monohydrate. After dilution with 35 ml. of water, the cooled reaction mixture afforded 0.140 g. (81%) of the keto ester III, m.p. 139.2–140.0°, which, by the criterion of mixture melting point, was identical with III as prepared above.

11,11-Dimethoxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene (V).—A solution of the ketal ester IV (2.293 g.) in purified tetrahydrofuran (35 ml.) was added to a slurry of lithium aluminum hydride (0.6 g.) in a mixture of ether (100 ml.) and tetrahydrofuran (20 ml.). After the reaction mixture had been stirred for 1.5 hr. at room temp., the excess hydride was decomposed with a limited quantity of water, and the mixture was filtered. After removal of solvent, there remained 1.979 g. (95%) of good-quality V as a white solid, m.p. 168.9–170.2°. Two recrystallizations from aqueous ethanol made basic with ammonia afforded the analytical sample as cubic crystals, m.p. 170.7–171.0°. In the infrared (KBr pellet) this material showed sharp absorption at 3555 cm.$^{-1}$ (hydroxyl) and no absorption in the carbonyl region.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 76.99; H, 6.80. Found: C, 76.96; H, 7.00.

11-Keto-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene (VI).—A solution of the ketal alcohol V (0.363 g.) in 11 ml. of acetone which contained 0.036 g. of *p*-toluenesulfonic acid monohydrate was heated under reflux for 4.5 hr. At the end of this time, the reaction mixture was poured into water. The oil which formed initially solidified after refrigeration and amounted to 0.279 g. (91%) of crude VI. The analytical sample, obtained after three recrystallizations from cyclohexane–benzene, had m.p. 139.6–140.0° and showed absorption in the infrared (10% soln. in chloroform) at 3400 (broad, hydroxyl) and 1710 cm.$^{-1}$ (sharp, ketone).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.45; H, 5.60.

11,11-Dimethoxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene (VII).—To the ketal alcohol V (1.36 g.) in 20 ml. of dry pyridine was added 1.350 g. of *p*-toluenesulfonyl chloride. After 17 hr. at room temperature the reaction mixture was poured into water and the solid which formed was filtered and washed well with water to give 2.093 g. (98%) of the ketal tosylate VII, m.p. 145° dec. The analytical sample was prepared by two recrystallizations from benzene–methanol and was obtained as a microcrystalline powder which, when put into the melting-point bath at 115°, underwent immediate decomposition. In the infrared (KBr pellet) it showed no absorption in the hydroxyl or carbonyl regions. It did, however, show strong sharp absorption at 1362, 1185 and 1173 cm.$^{-1}$, which, in the compounds we have examined, appears to be characteristic for *p*-toluenesulfonate esters.

Anal. Calcd. for $C_{26}H_{26}SO_5$: C, 69.32; H, 5.82. Found: C, 69.22; H, 5.80.

11-Keto-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene (VIII).—A mixture of the ketal tosylate VII (1.575 g.), acetone (50 ml.) and *p*-toluenesulfonic acid monohydrate (0.112 g.) was heated under reflux for 4 hr. and then diluted with water. There was obtained 1.288 g. (91%) of pure VIII as a white solid which had m.p. 167° without dec. This solid, on recrystallization from ethanol, gave material which had m.p. 152° dec. The infrared spectra (KBr pellets) of the two substances were identical and indistinguishable from those of the analytical samples. They possessed strong sharp absorption at 1719 (ketone) and 1358, 1189 and 1173 cm.$^{-1}$ (tosylate). The odd melting-point behavior was observed regularly and prompted duplicate analyses. Sample A was material of m.p. 167° which was then recrystallized three times from ethanol. Sample B was a portion of sample A which was dissolved in acetone and precipitated by the addition of water. After being dried, both samples yielded acceptable analyses.

Anal. Calcd. for $C_{24}H_{20}SO_4$: C, 71.25; H, 4.98. Found for sample A: C, 71.26; H, 5.07. Found for sample B: C, 71.26; H, 5.12.

After the analyses (10 days after their preparation) the two samples showed the following melting point behavior: sample A, m.p. 151° dec.; sample B, m.p. 166.5–167.5° dec.; mixture, m.p. 155–157° dec.

11-Keto-12-methylene-9,10-dihydro-9,10-ethanoanthracene (IX).—Exactly 26.2 g. of 0.0941 molal sodium hydroxide (0.00247 mole) was diluted to 50 ml. with water and added to a solution of keto tosylate VIII (1.000 g., 0.00248 mole, m.p. 151–152° dec.) in 200 ml. of purified dioxane. After 22 hr. at room temp., the solution was concentrated under reduced pressure to *ca.* 70 ml., diluted with 100 ml. of ether, washed successively with three 20-ml. portions of 10% aqueous sodium carbonate and then with water until the aqueous extracts were neutral, and finally dried over magnesium sulfate. The solid obtained by removal of solvent was recrystallized from ethanol to yield 0.441 g. of pure IX, m.p. 222.2–222.7°. A further 0.057 g. of IX, m.p. 223.0–223.2°, was obtained by concentration of the mother liquors, bringing the total yield to 0.498 g. (87%). Four recrystallizations from ethanol afforded the analytical sample as needles, m.p. 223.0–223.4°.[14]

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[13] Th. J. DeBoer and H. J. Backer, *Rec. trav. chim.*, **73**, 229 (1954).

[14] The melting point was dependent on the rate of heating; the value recorded was obtained on a sample inserted into the melting point bath just below its melting point.

Anal. Calcd. for $C_{17}H_{12}O$: C, 87.91; H, 5.21. Found: C, 88.00; H, 5.37.

In the infrared (KBr pellet), IX possessed strong, sharp absorption at 1706 and 1625 cm.$^{-1}$ (α,β-unsaturated ketone) and, among others, at 945 cm.$^{-1}$ (vinylketone). In the ultraviolet (95% ethanol), IX had: λ_{max} 285 (ϵ 3,800) and 343 (ϵ 730) mμ; λ_{min} 260 (ϵ 2,400) and 318 (ϵ 480) mμ; inflections at 247 (ϵ 5,400) and 274 (ϵ 3,200) mμ.

In another experiment, with reagents at the same concentrations as above, the course of the reaction was followed by titrating aliquots with standard acid. At room temperature, the reaction had a half-life of *ca.* one hour. When the reaction was conducted as above, but with an excess of base, the product was a complex mixture which was not resolved, but which did not contain (by infrared analysis) any significant quantity of the β-ketol VI.

Clemmensen Reduction of the β-Ketol VI.—A mixture of the β-ketol VI (0.325 g., m.p. 138–139°), glacial acetic acid (10 ml.) and zinc amalgam (from 5 g. of zinc which had been treated with concd. hydrochloric acid, aqueous mercuric chloride, and washed with water) was heated under reflux while a total of 7 ml. of concd. hydrochloric acid was added at 30-min. intervals over the course of 6 hr. At the end of this time, the mixture was filtered while still hot and the filtrate was diluted with water and extracted with ether which was washed with several portions of water. After removal of solvent from the ether extract there remained an oil which was carefully chromatographed on 40 g. of Florisil. Fraction A, an oil, was eluted with petroleum ether (60–68°) and amounted to 0.119 g. Fraction B, a glass, was eluted with 40% benzene in petroleum ether and amounted to 0.145 g. (40%) of crude acetate XV. After one recrystallization from ethanol, fraction B afforded pure XV, m.p. 119.0–119.8° (lit.[6] m.p. 122°), identical by the criteria of mixture melting point and infrared spectra with an authentic sample of XV prepared as described by Alder.[6]

Fraction A from the chromatography was distilled through a Kragen tube at 0.3 mm. and a pot temp. of 80–100° to give a semi-solid distillate which, after two recrystallizations from ethanol–water, afforded the analytical sample of the hydrocarbon XIII, m.p. 89–92°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.69; H, 7.32. Found: C, 92.49; H, 7.74.

The structure of XIII is tentative and is based on its mode of formation, its empirical formula, and its infrared spectrum (KBr pellet) which had no absorption (other than C–H) above 1500 cm.$^{-1}$ and possessed characteristic C-methyl absorption at 1372 and 1452 cm.$^{-1}$.

Lithium Aluminum Hydride Reduction of the Ketal Tosylate VII.[8]—A solution of the ketal tosylate VII (0.511 g.) in 20 ml. of dry tetrahydrofuran was added, over a period of 45 min., to a boiling solution of lithium aluminum hydride (0.3 g.) in 50 ml. of the same solvent. The mixture was held under reflux for an additional 7 hr., at the end of which time the excess hydride was decomposed with a limited amount of water. The mixture was filtered and the solvent was removed to yield 0.370 g. of a solid which was chromatographed on 44 g. of Florisil. Elution with benzene afforded, in distinct fractions, 0.118 g. of unreacted VII and 0.156 g. of a solid, m.p. 148–150° dec., which had an infrared spectrum identical to that of the ketal alcohol V. Recrystallization of this material from ethanol–water gave a white solid which, when put into the melting point bath at 140°, slowly decomposed and melted. It exhibited the same behavior on admixture with authentic V. Because of the ambiguous melting point, a portion of the white solid was *trans*-ketalized with acetone in the manner already described to give, directly, pure keto alcohol VI, m.p. 139.0–139.5°, identical, by the criteria of mixture melting point and infrared spectra, with authentic VI. Thus, there was isolated from the reaction a 23% yield of unreacted VII and a 48% yield of the ketal alcohol V. No other material was eluted in significant quantity from the column.

Clemmensen Reduction of Keto Tosylate VIII.—The reduction was conducted as with the ketol VI on 0.514 g. of the keto tosylate VIII and the oil (0.322 g.) obtained directly from the reaction was chromatographed on 40 g. of Florisil. With petroleum ether (60–68°) there was eluted 0.101 g. of an oil which was not identified, but which, by infrared examination, contained no identifiable structural unit other than C-methyl (absorption at 1376 cm.$^{-1}$) and was not identical with the oil (see above) from which the hydrocarbon XIII was isolated. Elution of the column with 10–50% benzene in petroleum ether afforded 0.129 g. of an oil which solidified on trituration with ethanol. Two recrystallizations of this solid from ethanol gave 0.013 g. of pure methyl ketone XII, m.p. 122.0–122.3° (lit. m.p. 121.6–122.4°,[4] 121.5–123°[7]), identical, by the criteria of mixture melting point and infrared spectra, with an authentic sample.[15] An additional 0.013 g. of XII, m.p. 120–121°, was obtained from the mother liquors, bringing the total yield to 10%.

Although the structure of the methyl ketone XII appeared correct, we obtained confirmatory evidence from its nuclear magnetic resonance spectrum. The spectrum was taken with a Varian Associates 40 megacycle dual purpose spectrophotometer on a 10% solution of XII in carbon tetrachloride with tetramethylsilane (*ca.* 1%) as the internal standard. Absorption occurred, in c.p.s. relative to the tetramethylsilane reference, at: −33 and −44 (12-CH_3); −88 (unresolved multiplet, 12-H); −168 and −171 (10-H); −187 (9-H); and −285 (aromatic hydrogens). Thus, all the hydrogen atoms were identified, and the intensities were, roughly, of the expected relative magnitudes.

Catalytic Reduction of Methylene Ketone IX.—The methylene ketone IX (0.112 g.) in 10 ml. of ethyl acetate was hydrogenated at atmospheric pressure in the presence of 30% palladium-on-charcoal (0.05 g.) as a catalyst. Hydrogenation was very rapid and was complete in less than 5 min. The catalyst was removed by filtration and, after removal of solvent, there was obtained, directly, 0.099 g. (88%) of pure methyl ketone XII, m.p. 120.0–120.6°, identical by the criteria of mixture melting point and infrared spectra, with authentic XII.

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(15) We are indebted to Prof. W. E. Noland for providing us with a sample of this material.