pyrrolidine enamine the time required for conversion, as well as the yield of the product, was the same as with gramine. In order to compare the utility of the enamine with that of the ketone, cyclohexanone and 2-methylcyclohexanone were refluxed with gramine under conditions identical with those of the enamine reaction. The endpoint was determined by cessation of the evolution of basic fumes as well as by the use of thin layer chromatography. It was found that this reaction required 5 days for completion and was less selective with respect to the site of alkylation as shown by the presence of several spots in the thin layer chromatograms of the crude product derived from 2-methylcyclohexanone.

Compound **10** (7a,8,10,11,11a,12-hexahydro-9H-benzo[*a*]xanthen-7a-ol) resulted from a spontaneous intramolecular hemiketalization of the primary product of the alkylation of the cyclohexanone pyrrolidine enamine with 1-dimethylaminomethyl-β-naphthol. That this conversion of the naphthol ketone to a hemiketal had taken place was indicated by the negative $FeCl_3$ color test for a phenolic hydroxyl, the insolubility of the compound in aqueous alkali, and the absence of a carbonyl band in the infrared spectrum.

Experimental[5]

General Procedure.—The reactions were carried out by refluxing 0.1 mole of pyrrolidine enamine of a ketone[6] with 0.1 mole of a Mannich base in 100 ml. of dioxane until, after *ca.* 24 hr., the evolution of basic fumes had subsided. After addition of 30 ml. of water, the reaction mixture was refluxed for 1 hr. and evaporated *in vacuo*. The residue was purified for analyses by distillation (compounds **1**, **2**, **5**, **6**, **7**, and **9**), by crystallization from ethanol (**4** and **10**) or ethyl acetate (**8**), and by chromatography on activated magnesium silicate (Florisil) 25 g./g. using ethyl acetate as eluent (**3**).

(5) Melting points were determined with the Thomas–Hoover capillary melting point apparatus which was calibrated against known standards. N.m.r. spectra were recorded in deuterated chloroform with tetramethylsilane as an internal reference using a Varian A-60 spectrometer. The thin layer chromatography was performed using silica gel G according to Stahl (Merck, Darmstadt) as the absorbent and ethanol as the eluent. Chromatograms were developed by spraying with aqueous $KMnO_4$. The authors are indebted to the Analytical and Physical Chemistry Department under the supervision of Mr. A. D. Lewis. In particular we wish to thank Mr. R. DeSimone and Mr. R. Puchalski for the spectral data and Mrs. U. Zeek for analytical determinations.

(6) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrel, *J. Am. Chem. Soc.*, **85**, 207 (1963).

The Pyrolysis of Acetylazo Compounds[1]

COLIN G. PITT

The Natural Products Laboratory, Research Triangle Institute, Durham, North Carolina

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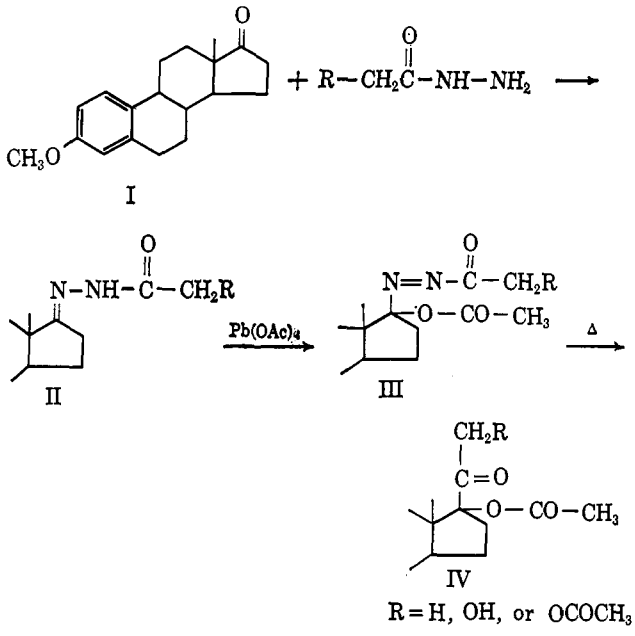
Aliphatic azo compounds are generally thought to decompose thermally by the simultaneous rupture of both carbon–nitrogen bonds, to form molecular nitrogen and two carbon radicals.[2,3] The subsequent behavior of the two radicals depends primarily on their structures and may be recombination, disproportionation, or abstraction of a proton from the solvent.[3] Wieland[4] has shown that, in the case of acetylazotriarylmethanes, radical recombination is dominant, and the major product of pyrolysis is the acetyltriarylmethane. More recently Freeman[5] has demonstrated that 3-acetoxy-Δ^1-pyrazoline, an α-acetoxyazoalkane, behaves similarly affording acetoxycyclopropane in good yield. We have sought to combine these two observations in attempting a simple synthesis of the cortical side chain from steroidal 17-ketones. While



this synthesis proved unsuccessful, our results do illustrate some interesting aspects of the behavior of radicals derived from the pyrolysis of azo compounds.

As a model for the proposed synthesis, we chose to study the conversion of estrone 3-methyl ether (I) into the corresponding 17-acetoxy-17-acetyl derivative IV (R = H). Accordingly, estrone 3-methyl ether was treated with acetylhydrazine, to form the acetylhydrazone II (R = H). This was converted to the 17-acetoxy-17-acetylazo steroid III (R = H) by reaction with lead tetraacetate, following the procedure developed by Iffland.[6] Elemental analysis, nuclear magnetic resonance (n.m.r.), and infrared spectral analysis showed the introduction of an acetoxy group, and were consistent with the formulation of our product as III (R = H). The stereochemistry of the substituents at C-17 is not known, although by analogy with other additions to 17-ketones, introduction of an α-acetoxy group would seem most probable. The spectral properties of the parent $-N{=}N-\underset{|}{C}{=}O$ group [λ_{max} 223 mμ (ε 1560), 317 mμ (ε 162)[7]] do not appear to have been reported previously; it is interesting to note the resemblance to the $-\underset{|}{C}{=}\underset{|}{C}-\underset{|}{C}{=}O$ chromophore.

(1) This work was carried out under Contract SA-43-ph-4351 of the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health.

(2) S. Seltzer, *J. Am. Chem. Soc.*, **85**, 14 (1963); **83**, 2625 (1961).

(3) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

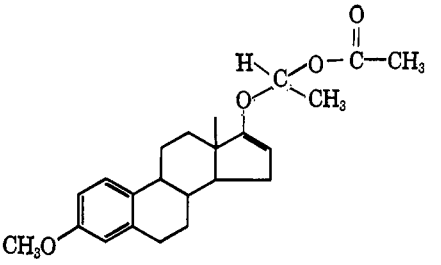
(4) H. Wieland, T. Ploetz, and H. Indest, *Ann.*, **532**, 166 (1937).

(5) J. P. Freeman, *J. Org. Chem.*, **29**, 1379 (1964).

(6) Iffland has shown that lead tetraacetate will convert alkylhydrazones into the corresponding α-acetoxyazoalkanes: D. C. Iffland, L. Salisbury, and W. R. Schafer, *J. Am. Chem. Soc.*, **83**, 747 (1961).

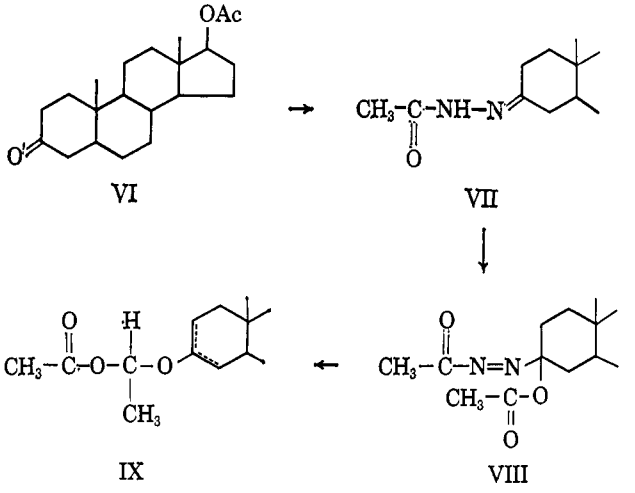
(7) The ultraviolet spectrum of III is complicated by the aromatic A ring absorption. These figures refer to the androstane VIII.

The azo compound III (R = H) was pyrolyzed in refluxing xylene for 1 hr. Formation of biacetyl in the reaction mixture was clearly indicated by its odor and the appearance of absorption bands at 423 and 447 mμ. After evaporation of the xylene, elution from alumina afforded estrone 3-methyl ether (40.6%) and a second component V (40.3%) as the major nonvolatile reaction products. The latter analyzed correctly for loss of 1 mole of nitrogen, but when dissolved in aqueous methanol containing hydrochloric acid it was converted to estrone 3-methyl ether, acetic acid, and acetaldehyde. The infrared spectrum of V showed the presence of an acetoxy group, while the n.m.r. spectrum showed singlets at 55 (18-CH_3), 125 (3H, $OCOCH_3$), and 228 (3-OCH_3), a doublet (J = 5 c.p.s.) at 88 and 93 (CH_3CH), a one-proton quartet (J = 5 c.p.s.) at 370, 375, 380, and 385 (CH_3CH), and a broad, one-proton singlet centered at 273 c.p.s. ($OC{=}CH$). On the basis of this evidence we formulate the pyrolysis product V as



V

In order to determine whether the course of the pyrolysis was influenced by the sterically crowded environment[8] at C-17, we repeated the reaction sequence at the C-3 position, using androstan-17β-ol-3-one acetate (VI). When the azo compound VIII

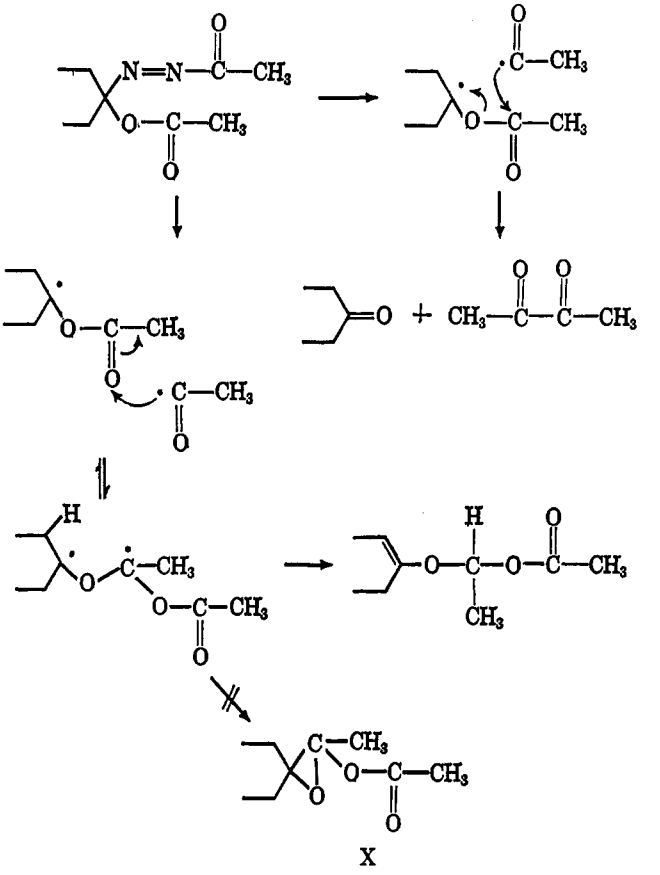


VI VII IX VIII

was pyrolyzed in boiling xylene, no androstan-3-one 17β-acetate was formed. The sole product (>95%) of the pyrolysis was identified as IX[9] on the basis of elemental and spectral analysis and its hydrolysis to androstan-17β-ol-3-one acetate when treated with hydrochloric acid in aqueous ethanol.

(8) E. J. Corey and W. Oppolzer, *J. Am. Chem. Soc.*, **86**, 1899 (1964).

(9) The position of the double bond is not established. Pyrolysis of VIII in acetic anhydride and in dimethylformamide also give the same product.



X

Figure 1.

Photolysis of the azo compounds III and VIII in methanol using a filter to exclude light of wave length <3500 Å. produced in each case a complex mixture of products which was not further investigated.

Discussion

The formation of rearranged products from the pyrolysis of azo compounds is not without precedent. For example the thermal decomposition of azobisisobutyronitrile is now known to produce a ketenimine as an intermediate.[10] The decomposition of 2,2′-azobiscyclopropylpropionitrile is reported[11] to give 1-methylcyclopenten-5-one azine as well as the expected product, 2,3-dicyclopropyl-2,3-dicyanobutane.

The formation of estrone 3-methyl ether from the pyrolysis of the azo compound III (R = H) is interpreted as the reverse of the addition of an acyl radical to the oxygen atom of a carbonyl group,[12] and may be assisted by an acetyl radical (Figure 1).

The formation of the enol ethers (V and IX) is less easy to understand, although a mechanism involving addition of the acetyl radical to the acetoxy group may be formulated as shown in Figure 1. The oxirane X can be ruled out as an intermediate since such compounds are known[13] to decompose thermally to α-acetoxy methyl ketones. The formation of the enol ether IX, to the exclusion of the 3-ketone in the andro-

(10) P. Smith, J. E. Sheats, and P. E. Miller, *J. Org. Chem.*, **27**, 4053 (1962), and references listed therein.

(11) C. G. Overberger, M. Tobkes, and A. Zweig, *ibid.*, **28**, 620 (1963).

(12) R. L. Huang and H. H. Lee, *J. Chem. Soc.*, 2500 (1964).

(13) J. D. Cocker, H. B. Henbest, G. H. Phillipps, G. P. Slater, and D. A. Thomas, *ibid.*, 6 (1965).

stane series may reflect the greater steric accessibility of the acetate carbonyl group or the relative ease of formation of the Δ^2 as opposed to the Δ^{16} double bond.

Experimental

Infrared spectra were measured with a Perkin-Elmer Model 221 spectrophotometer. N.m.r. spectra were obtained using a Varian A-60 spectrometer with samples dissolved in deuteriochloroform (internal standard tetramethylsilane). Ultraviolet spectra were obtained using a Bausch and Lomb Model 505 spectrophotometer. Thin layer chromatograms were run on plates coated with silica gel G, and developed with 5% phosphomolybdic acid in ethanol. Melting points are not corrected. The elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Acetylhydrazine.—Ethyl acetate (17.6 g., 0.2 mole) was added in portions over a period of 30 min. to anhydrous hydrazine (9.6 g., 0.3 mole), while refluxing the mixture on a steam bath. After heating the reaction mixture for a further 4 hr., unchanged starting materials were removed *in vacuo*. The acetylhydrazine remained as a hygroscopic, white, crystalline solid and was not further purified.

Acetylhydrazone of Estrone 3-Methyl Ether.—Estrone 3-methyl ether (4.000 g., 14.07 mmoles) and acetylhydrazine (2.00 g., 27.0 mmoles) in dimethylformamide (50 ml.) were heated on a steam bath overnight. On cooling to room temperature the product separated as white needles which were filtered, washed with methanol, and dried *in vacuo*. Thin layer chromatography (t.l.c.) indicated that the product was homogeneous: yield 3.526 g. (73.6%). An analytical sample was obtained by crystallization from a chloroform and ethanol mixture: m.p. 232–233° (capillary, varies with rate of heating); $\nu_{max}^{CHCl_3}$ 3355 (NH) and 1660 cm.$^{-1}$ (NHC=O); and $\lambda_{max}^{CH_3OH}$ 231 mμ (ϵ 21,500), 278 (2070), and 287 (1810). In addition to the absorption of the steroid nucleus, the n.m.r. spectrum showed singlets at 55 (18-CH_3), 136 (CH_3C=O), and 228 c.p.s. (OCH_3).

Anal. Calcd. for $C_{21}H_{28}N_2O_2$: C, 74.08; H, 8.29; N, 8.23. Found: C, 74.35; H, 8.44; N, 8.44.

Reaction of Lead Tetraacetate and the Acetylhydrazone of Estrone 3-Methyl Ether.—Recrystallized lead tetraacetate (2.733 g., 6.164 mmoles) in methylene chloride (20 ml.) was added dropwise to a stirred slurry of the acetylhydrazone (2.000 g., 5.875 mmoles) in methylene chloride (25 ml.) under a nitrogen atmosphere. The reaction temperature was regulated by a water bath at room temperature. After addition was complete, the reaction mixture was stirred for 20 min., when unchanged lead tetraacetate was decomposed with ethylene glycol (0.5 ml.). Lead diacetate was removed by filtration, and the filtrate was washed with aqueous sodium bicarbonate (two 25-ml. portions), and water. After drying over anhydrous magnesium sulfate, the solvent was evaporated to leave 2.590 g. of a colorless oil. The oil was dissolved in ether (50 ml.), filtered to remove unchanged starting material (102.5 mg.), and cooled to −10°. The white crystals (816 mg.) which separated were filtered and dried. T.l.c. indicated that the crystals were homogeneous. The mother liquors were evaporated, and the residue was crystallized from methanol, to give an additional 476 mg. of the pure product, yield 55.2%.

An analytical sample, obtained by recrystallization from methanol, melted at 142° dec. (capillary); $\nu_{max}^{CS_2}$ 1765 (–N=NC=O, $OCOCH_3$), and 1245 and 1210 cm.$^{-1}$ ($OCOCH_3$); and $\lambda_{max}^{95\%\ EtOH}$ 226 mμ (ϵ 7520), 278 (2050), 287 (1850), and 314 (197). In addition to the absorption of the steroid nucleus, the n.m.r. spectrum showed singlets at 76 (18-CH_3), 118 and 122 ($OCOCH_3$ and N=$NCOCH_3$), and 226 c.p.s. (OCH_3).

Anal. Calcd. for $C_{23}H_{30}N_2O_4$: C, 69.32; H, 7.59; N, 7.03. Found: C, 69.26; H, 7.55; N, 7.16.

Pyrolysis of III.—A solution of III (400 mg.) in xylene (40 ml.) was refluxed for 1 hr. under a nitrogen atmosphere. T.l.c. of the reaction mixture showed two major steroidal products. The presence of biacetyl was indicated by its characteristic odor and absorption (λ_{max}^{xylene} 423 and 447 mμ). The xylene was evaporated under reduced pressure, and the residual oil was eluted from neutral alumina (grade III, 30 g.) with carbon tetrachloride. The more polar component was identified as estrone 3-methyl ether (116 mg., 40.6%) by its infrared spectrum and mixture melting point. The second component V (150 mg., 40.3%) melted at 114–119° (Kofler) when crystallized from methanol: $\nu_{max}^{CS_2}$ 1750 and 1770 (C=O), 1265, 1250, and 1230 cm.$^{-1}$ ($OCOCH_3$) (the absorption at 1770 cm.$^{-1}$ was approximately half the intensity of the band at 1750 cm.$^{-1}$); and λ_{max} 223 mμ (ϵ 6860), 278 (2140), and 287 (1860). In addition to the absorption of the steroid nucleus, the n.m.r. spectrum showed singlets at 55 (18-CH_3), 125 ($OCOCH_3$), and 228 (OCH_3), a doublet (J = 5 c.p.s.) at 88 and 93 (CH_3CH), a one-proton quartet (J = 5 c.p.s.) at 370, 375, 380, and 385 ($HCCH_3$), and a broad, one-proton singlet centered at 273 c.p.s. (OC=CH).

Anal. Calcd. for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.46; H, 8.16; N, <0.2.

Hydrolysis of V.—To a solution of V (82 mg.) in methanol (25 ml.) and water (5 ml.) was added 1 drop of hydrochloric acid. After standing at room temperature for 45 min., approximately 15 ml. of the solvent was distilled into a solution of 2,4-dinitrophenylhydrazine (53 mg.) in methanol (20 ml.). The undistilled reaction mixture was neutralized with 0.1 *M* aqueous sodium hydroxide (3.3 ml.), and then evaporated to dryness *in vacuo*. The residual solid was extracted with chloroform (three 20-ml. portions) and filtered. The filtrate was evaporated to dryness, to give estrone 3-methyl ether (60 mg., 95.3%), identified by its infrared spectrum and mixture melting point. The chloroform insoluble material (26 mg.) was shown by its infrared and n.m.r. spectrum to contain approximately 20% of sodium acetate, yield 30%.

The 2,4-dinitrophenylhydrazine solution was evaporated to dryness and the residue was fractionally crystallized from ethanol and water. Although t.l.c. indicated the presence of the 2,4-dinitrophenylhydrazone of acetaldehyde, a pure sample of this material could not be isolated.

In a second experiment, 2,4-dinitrophenylhydrazine (100 mg.) in methanol[14] (20 ml.) and water (2 ml.) containing 2 drops of hydrochloric acid was added to V (47.6 mg.). After standing at room temperature for 3.5 hr., the reaction mixture was filtered to remove the 2,4-dinitrophenylhydrazone of estrone 3-methyl ether (51 mg.). The filtrate was evaporated and the residue was eluted from Florisil to afford 15.7 mg. (55%) of the 2,4-dinitrophenylhydrazone of acetaldehyde, identified by its infrared spectrum and mixture melting point.

Acetylhydrazone of Androstan-17β-ol-3-one Acetate.—A solution of the ketone (3.000 g., 9.025 mmoles) and acetylhydrazine (1.5 g., 20 mmoles) in ethanol (35 ml.) was refluxed for 1 hr. The resulting slurry was allowed to cool to room temperature, and then filtered. The solid which had separated was filtered, washed with methanol, and dried *in vacuo*. T.l.c. indicated that the product was homogeneous: yield 2.961 g. (84.5%); m.p. 232–243° (capillary, dependent on rate of heating); $\nu_{max}^{CHCl_3}$ 3365 (NH), 1725 ($OCOCH_3$), 1665 ($NHCOCH_3$), and 1260 ($OCOCH_3$); and $\lambda_{max}^{CH_3OH}$ 236 mμ (ϵ 10,900). In addition to the absorption of the steroid nucleus, the n.m.r. spectrum showed singlets at 49 (18-CH_3), 56 (19-CH_3), 222 ($OCOCH_3$), and 235 ($NCOCH_3$), and a one-proton multiplet at 265–290 c.p.s. (17β-$CHOCOCH_3$).

Anal. Calcd. for $C_{23}H_{35}N_2O_3$: C, 71.10; H, 9.34; N, 7.21. Found: C, 71.17; H, 9.54; N, 6.95.

Reaction of the Acetylhydrazone of Androstan-17β-ol-3-one Acetate with Lead Tetraacetate.—Recrystallized lead tetraacetate (4.926 g., 11.11 mmoles) in methylene chloride (40 ml.) was added dropwise to a stirred slurry of the acetylhydrazone (3.886 g., 10.00 mmoles) in methylene chloride (50 ml.) under a nitrogen atmosphere. The reaction temperature was regulated by a water bath at room temperature. After the addition was complete, the reaction mixture was stirred for 15 min., when ethylene glycol (0.5 ml.) was added to decompose unchanged lead tetraacetate. Lead diacetate was removed by filtration, and the filtrate was washed with aqueous sodium bicarbonate (two 30-ml. portions) and saturated aqueous sodium chloride. After drying over anhydrous magnesium sulfate, the solvent was evaporated to leave 5.079 g. of a yellow oil of purity greater than 95% as judged by t.l.c. Crystallization of the oil from hexane (40 ml.) gave 2.732 g. of white nodules, m.p. 121–133° dec. (capillary). Concentration of the mother liquors afforded an additional 584 mg. of the product, m.p. 109–140° dec., ex-

(14) Mallinckrodt analytical reagent. In a blank experiment, analysis by t.l.c. showed that the solvent system was not the source of the 2,4-dinitrophenylhydrazone of acetaldehyde.

hibiting an identical infrared spectrum. The melting point range and the difficulty in obtaining crystals suggested the product was a mixture of C-3 epimers. This explanation was strengthened by the n.m.r. spectrum, which showed singlets at 48 (18-CH_3) and 122 (six protons, 17β-$OCOCH_3$ and N=$NCOCH_3$), a broad singlet at 56 (19-CH_3), a doublet at 115.5 and 117 (equal mixture of 3α- and 3β-$COCOCH_3$), and a multiplet at 266–287 c.p.s. (1 proton, 17β-C*H*$OCOCH_3$); $\nu_{max}^{CS_2}$ 1760 and 1740 ($OCOCH_3$, N=N$COCH_3$), 1250, and 1225 ($OCOCH_3$); and $\lambda_{max}^{95\%\ EtOH}$ 223 mμ (ϵ 1560) and 317 mμ (ϵ 162).

Anal. Calcd. for $C_{25}H_{38}N_2O_5$: C, 67.23; H, 8.58; N, 6.27. Found: C, 67.04; H, 8.57; N, 6.41.

Pyrolysis of VIII.—A solution of VIII (446 mg.) in xylene (45 ml.) was refluxed under a nitrogen atmosphere for 45 min. The solvent was evaporated under reduced pressure, to leave a solid residue of purity greater than 95% as judged by t.l.c. Crystallization of the residue from methanol (30 ml.) at −10° afforded 210 mg. of white crystals: m.p. 120–151° (capillary); $\nu_{max}^{CS_2}$ 1740 ($OCOCH_3$), 1670 (C=CO), and 1250 cm.$^{-1}$ ($OCOCH_3$). The ultraviolet spectrum showed only end absorption. The n.m.r. spectrum showed singlets at 48 (six protons, 18-CH_3, 19-CH_3), 122, and 124 (two $OCOCH_3$ groups), a doublet (J = 5 c.p.s.) at 85 and 90 (C*H*$_3$CH), a quartet (J = 5 c.p.s.) at 370, 375, 380, and 385 (*H*CCH_3), a multiplet at 275 to 290 (17β-C*H*$OCOCH_3$), and a broad, one-proton singlet centered at 266 c.p.s. (OC=C*H*).

Anal. Calcd. for $C_{25}H_{38}O_5$: C, 71.74; H, 9.15; N, 0.00. Found: C, 71.99; H, 9.17; N, 0.15 ± 0.3.

Hydrolysis of the Pyrolysis Product IX.—A solution of IX (50 mg.) in warm ethanol (10 ml.) was diluted with water (4 ml.) and 3 drops of hydrochloric acid. After standing at room temperature for 1 hr. the solvent was evaporated under reduced pressure. The white, crystalline residue was identified as pure androstan-17β-ol-3-one acetate by t.l.c., infrared, and n.m.r. spectral analysis.

Acknowledgment.—We take pleasure in thanking Dr. M. E. Wall, director of this laboratory, for his encouragement and advice.

Rearrangement. II. Pyrolysis and Acetolysis of Cyclohexanemethyl *p*-Toluenesulfonate

RYOTARO KOTANI[1] AND SHIRO SATOH[2]

Research Laboratory, Kureha Spinning Company, Ltd., Takatsuki, Osaka, Japan

Received April 5, 1965

The pyrolysis of some cyclohexanemethyl derivatives has been investigated by several groups of workers in recent years. Two different mechanisms have been reported: one a *cis* elimination giving exclusively methylenecyclohexane, and the other a carbonium ion type reaction giving isomeric cycloalkenes. The former is patterned after the widely accepted proposal of Hurd and Blunck[3] for carboxylic esters, involving a quasi, six-membered ring as a transition state and adapted in the cyclohexane series for the pyrolysis of cyclohexanemethyl acetate[4] and N,N-dimethylcyclohexanemethylamine oxide.[4,5] The latter involves the pyrolysis of cyclohexanemethyl borate.[6] No comparable experiments have yet been made for the pyrolysis of cyclohexanemethyl *p*-toluenesulfonate (I).[7]

The recrystallized I, when heated to 200° at reduced pressure under nitrogen, readily decomposed. The crude product, collected in a Dry Ice cooled trap, was analyzed by gas chromatography. Each component was separated by preparative-scale gas chromatography and identified by comparison of its n.m.r. spectrum and gas chromatographic relative retention time with those of an authentic sample. The product consisted of 1-methylcyclohexene (56.6%), 3-methylcyclohexene (8.9%), methylenecyclohexane (1.1%), cycloheptene (6.5%), cyclohexene (2%), methylcyclohexane (20.4%), and toluene (4.5%).

Pyrolytic *cis* elimination of I would be expected to give predominantly methylenecyclohexane, as observed in the runs with the above acetate and amine oxide. The analysis, however, revealed only 1.1% of methylenecyclohexane in the products. Rearranged compounds predominated, instead. The fact that 1-methylcyclohexene is thermodynamically more stable than methylenecyclohexane[8] may suggest that the latter, formed initially by *cis* elimination of I, subsequently might have rearranged to the former during reaction. This possibility was excluded by a control experiment showing that isomerization of exocyclic to endocyclic double bonds scarcely occurred under the experimental conditions employed. The possibility that the pyrolysis proceeds through a *cis* elimination mechanism, hence, may be eliminated. Unexpectedly, the saturated compound methylcyclohexane was formed in fairly high yield in contrast to its nonformation as reported in the pyrolysis of the acetate, amine oxide, and borate. The formation of the rearranged–unrearranged cycloalkenes might be explained in terms of either carbonium ions or free radicals, whereas with the formation of the saturated compound carbonium ion disproportionation might be less favorable than radical-pair disproportionation in some respects under the experimental conditions used. Abstraction of a hydride from a carbonium ion would give a carbonium ion with two positive charges. A similar, unfavorable situation would result if a hydride is abstracted from the cyclohexanemethyl group in I, followed by the breaking of the C–O bond. It seems also unlikely to assume hydride abstraction by carbonium ion from the *p*-toluenesulfonate group. There was no diolefinic hydrocarbon found which might be formed by abstraction of a hydride from an olefinic hydrocarbon, followed by loss of a proton. No hydride donor was added to the reaction system, but hydrides might be available from some other decomposed fragments. Further discussion on the mechanism should not be given without further experimental evidence, but it is likely that the pyrolysis might proceed partially, if not predominantly, through pathways other than those reported by previous workers.[4–6] Further experiments are being carried out to elucidate its nature.

Toluene might be formed from cyclohexanemethyl and/or *p*-toluenesulfonate groups. Numerous investi-

(1) To whom inquiries should be addressed.

(2) Responsible for n.m.r. analysis.

(3) C. D. Hurd and F. H. Blunck, *J. Am. Chem. Soc.*, **60**, 2419 (1938).

(4) H. E. Baumgarten, F. A. Bower, and T. T. Okamoto, *ibid.*, **79**, 3145 (1957).

(5) A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *ibid.*, **79**, 4729 (1957).

(6) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4193 (1961).

(7) J. Blackwell and W. J. Hickinbottom [*J. Chem. Soc.*, 366 (1963)] have reported that isomerization of the cyclohexanemethyl group to 1-methylcyclohexyl occurred during alkylation of the aromatic nuclei by the thermal decomposition of I in toluene and phenol.

(8) (a) R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **79**, 253 (1957); **80**, 1424 (1958); (b) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *ibid.*, **81**, 3153 (1959).