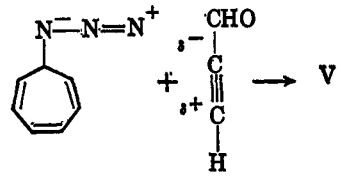
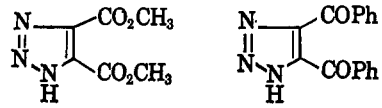


position on the basis of the polarization of the reactants and the mechanism of dipolar addition.[7]

The ability of the cycloheptatrienyl group to leave a carbon, nitrogen, or oxygen atom has been established.[8] The adducts III, IV, and V would be expected to undergo a similar displacement in acid. When compounds III and IV were treated with hydrogen chloride in ether, tropylium chloride separated and triazoles VI and VII were isolated from the respective solutions.



VI VII

Cleavage probably occurred by protonation of the substituted nitrogen atom, with subsequent loss of the organic cation. Triazole V did not give a cleavage product under these conditions.

Experimental

7-Azido-1,3,5-cycloheptatriene[1] (I).—A solution of 7.1 g. (0.040 mole) of tropylium tetrafluoroborate in 60 ml. of water was stirred while a solution of 3.0 g. (0.046 mole) of sodium azide in 10 ml. of water was added dropwise. An oil separated which was extracted into benzene or methylene chloride. The extract was washed with water, dried, concentrated, and distilled immediately, b.p. 36–40° (0.1 mm.). Redistillation gave 3.0 g. (56%), b.p. 70–72° (7 mm.), $n^{25}D$ 1.5461 [lit.[1] b.p. 50° (1 mm.), $n^{25}D$ 1.5466]. The infrared spectrum showed the presence of the azide group at 2120 cm.$^{-1}$. On standing at 25°, a solid separated and the liquid became black. The azide could be stored for short periods (24 hr.) at −10° under nitrogen.

When methyl tropyl ether[3] was allowed to stand overnight in an ether solution of excess hydrazoic acid, no solid separated.

1-(2,4,6-Cycloheptatrienyl)-4,5-dicarbomethoxy-1,2,3-triazole (III).—A solution of 1.7 g. (0.013 mole) of freshly distilled tropylium azide and 1.8 g. (0.013 mole) of dimethyl acetylenedicarboxylate in 10 ml. of carbon tetrachloride was heated carefully on a steam bath until the initial evolution of heat stopped. After an additional 30 min. of heating at reflux, the solvent was removed and the residue was recrystallized from ligroin–ether; yield 2.6 g., 73%, m.p. 63–64°.

Anal. Calcd. for $C_{13}H_{13}N_3O_4$: C, 56.7; H, 4.8; N, 15.3. Found: C, 56.5; H, 4.7; N, 15.2.

The product was obtained in 64% yield (7.0 g.) when undistilled tropylium azide, from 7.1 g. (0.040 mole) of tropylium tetrafluoroborate and 3.0 g. (0.046 mole) of sodium azide, was heated for 2 hr. with 5.6 g. (0.040 mole) of dimethyl acetylenedicarboxylate in 60 ml. of carbon tetrachloride.

4,5-Dicarbomethoxy-1,2,3-triazole[9] (VI).—A solution of 3.5 g. (0.013 mole) of 1-(2,4,6-cycloheptatrienyl)-4,5-dicarbomethoxy-1,2,3-triazole (III) in 100 ml. of ether was treated with hydrogen chloride for 1 hr. and the tropylium chloride which separated was collected; yield, 1.7 g. (100%). The filtrate was washed with water, dried, concentrated, and recrystallized from benzene to give 0.8 g. (34%), m.p. 129–130° (lit.[9] m.p. 133°).

Anal. Calcd. for $C_6H_7N_3O_4$: C, 39.0; H, 3.8; N, 22.7. Found: C, 39.1; H, 3.9; N, 23.0.

1-(2,4,6-Cycloheptatrienyl)-4,5-dibenzoyl-1,2,3-triazole (IV).—Tropylium azide was prepared from 2.0 g. (0.031 mole) of sodium azide and 5.0 g. (0.028 mole) of tropylium tetrafluoroborate and extracted into 50 ml. of benzene. After drying, 3.5 g. (0.015 mole) of dibenzoylacetylene was added and the mixture was heated for 2 hr. on a steam bath. Removal of the solvent and recrystallization of the residue from ethanol gave 3.2 g. (58%), m.p. 75–77°.

Anal. Calcd. for $C_{23}H_{17}N_3O_2$: C, 75.2; H, 4.7; N, 11.4. Found: C, 74.9; H, 4.5; N, 11.4.

4,5-Dibenzoyl-1,2,3-triazole (VII).—Hydrogen chloride was passed through a solution of 1.0 g. (0.0027 mole) of 1-(2,4,6-cycloheptatrienyl)-4,5-dibenzoyl-1,2,3-triazole (IV) in 100 ml. of ether for 30 min. and the residue was collected (0.34 g., 100%, tropylium chloride). The filtrate was concentrated, washed with water, and dried to give 0.75 g. (100%) of the triazole VII, m.p. 164–165°. This compound has been previously reported but with no mention of the preparation or the melting point.[10]

The triazole VII was also obtained in 13% yield by allowing 2.3 g. of dibenzoylacetylene to stand for 2 days at room temperature with an excess of hydrazoic acid in benzene–ether. The product melted at 164–165° after recrystallization from ethanol and did not depress the melting point of material obtained from IV.

Anal. Calcd. for $C_{16}H_{11}N_3O_2$: C, 69.3; H, 4.0; N, 15.2. Found: C, 69.0; H, 4.0; N, 15.3.

1-(2,4,6-Cycloheptatrienyl)-4-formyl-1,2,3-triazole (V).—Tropylium azide was prepared from 6.0 g. (0.092 mole) of sodium azide and 14.0 g. (0.080 mole) of tropylium tetrafluoroborate and extracted into methylene chloride. The organic extract was dried, concentrated, and taken up in a solution of 4.3 g. (0.089 mole) of propargyl aldehyde in 50 ml. of carbon tetrachloride. The solution was heated on a steam bath for 2 hr. and concentrated, and the residue was distilled to give 10.0 g. (67%) of product, b.p. 92–94° (0.07 mm.), $n^{25}D$ 1.5750.

Anal. Calcd. for $C_{10}H_9N_3O$: C, 64.1; H, 4.9; N, 22.4; mol. wt., 187. Found: C, 64.2; H, 4.9; N, 22.2; mol. wt., 187 (mass spectra).

Attempted Preparation of 4-Formyl-1,2,3-triazole.—Hydrogen chloride was passed through a solution of 5.0 g. of 1-(2,4,6-cycloheptatrienyl)-4-formyl-1,2,3-triazole (V) in 100 ml. of ether for 30 min. The solid was collected and the filtrate was washed with water, dried, and concentrated. A small amount of unidentifiable oil remained.

Attempted Condensation of Diphenylacetylene and Phenylacetylene with Tropylium Azide.—A solution of 6.7 g. (0.050 mole) of tropylium azide and 8 g. (0.045 mole) of diphenylacetylene in benzene was heated at reflux for 3 days. Removal of the solvent and distillation of the residue gave 7.5 g. (94%) of unchanged diphenylacetylene. When toluene was used as a solvent and the reaction time was 24 hr., 70% of the starting material was recovered unchanged.

Phenylacetylene and tropylium azide (0.02 mole of each) were heated in benzene at reflux for 2 hr. Upon distillation, 64% of the azide was recovered. No higher-boiling material remained in the flask.

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17-Azasteroids. III.[1] The Synthesis of N-Hydroxy-17a-aza-D-homosteroids

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Recent publications[2–4] from this laboratory described the synthesis of various 17-azasteroids. It was of

(1) This work was supported, in part, by a National Institutes of Health Grant H-5266.
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Figure 1.

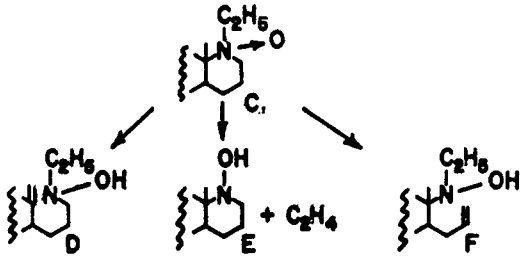

Figure 2.

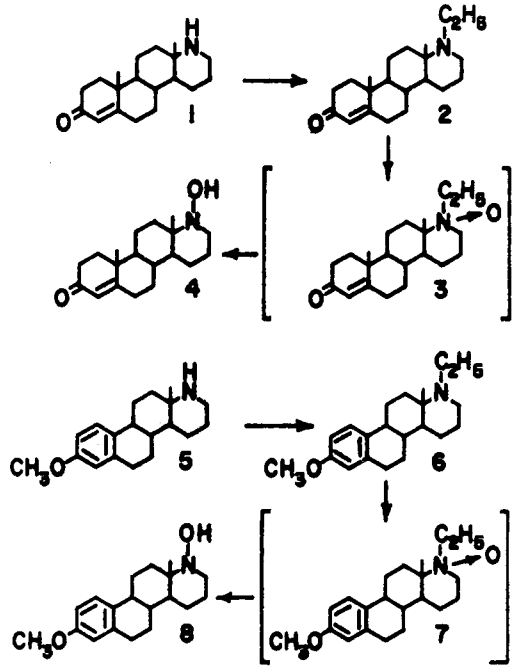

Figure 3.

interest to prepare an azasteroid which had a negative group attached to the nitrogen in order to test the feasibility of such a synthesis. A steroidal heterocyclic hydroxylamine of the type A (Figure 1) has not been reported in the literature, except hydroxamic acids of the type B which were synthesized by the Schering group and reported by Robinson and co-workers.[5] Extensive work has been done on the synthesis of the substituted hydroxylamines by thermal decomposition of the corresponding amine oxides.[6] Although utilization of this reaction has been exhaustively investigated for the synthesis of olefins and substituted acyclic hydroxylamines, not much work seems to have been done in the area of heterocyclic amines. Pyrolysis of N-ethyl and N-methyl tetrahydroquinoline oxide are reported[7] to yield tetrahydroquinoline together with acetaldehyde and formaldehyde, respectively. Cope[8] has reported formation of a ring-cleaved unsaturated hydroxylamine and a saturated bicyclic compound upon thermal decomposition of N-methyl-α-picoline oxide. However, Thesing[9] obtained the desired N-hydroxypyrrolidine by pyrolyzing N-ethylpyrrolidine oxide. Rogers[10] described the synthesis of substituted acyclic hydroxylamines as well as some heterocyclic hydroxylamines which involved a reverse Michael-type reaction on oxides of compounds of the type $R_2NCH_2CH_2X$ (X = COOR', CN, or COPh).

In this note we intend to describe the synthesis of two N-hydroxy-17a-aza-D-homosteroids, which were prepared by the thermal decomposition of the oxide of the corresponding N-ethyl derivatives. These oxides in turn were prepared in good yield by treating the appropriate N-ethyl compounds with *m*-chloroperbenzoic acid. Decomposition of the N-oxides of the type C could, however, yield ring-cleaved unsaturated hydroxylamines of the types D and F along with the expected hydroxylamine E and ethylene. When the amine oxides **3** and **7** were pyrolyzed by refluxing them in xylene under nitrogen, only single products were obtained in each case which were subsequently proved to be the desired N-hydroxy compounds **4** and **8**, respectively. Proof of structure of these compounds as well as of the intermediates, was provided by their n.m.r. spectra. The n.m.r. spectra of the N-ethyl derivatives **2** and **6** showed a signal for three proton triplet centered at 60 c.p.s. for the C-21 methyl group and the C-18 methyl protons appeared at 52.5 c.p.s. In the pyrolyzed product there was no signal for the C-21 methyl group and inspection of the low-field region of the spectra revealed only one vinylic proton around 345 c.p.s. Alternate structures D or F for the pyrolyzed product would have shown signals for C-21 methyl and also two additional vinylic protons in the low field region of the spectra. The C-18 methyl protons in the hydroxylamines appeared as expected at a low field of 62.5 c.p.s. Moreover, the elemental analysis of the products corresponded for the hydroxylamine structures **4** and **8**.

Thus, this sequence of reactions provides an entry into a new class of compounds and could possibly be extended to other azasteroids (Figures 2 and 3).

Experimental[11]

N-Ethyl-17a-aza-D-homoandrost-4-en-3-one (2).—To a solution of 1.00 g. of 17a-aza-D-homoandrost-4-en-3-one (1)[12] in 30 ml. acetone was added 0.9 g. of diethyl sulfate and a solution of 1 g. of potassium hydroxide in 3 ml. of water. The mixture was heated under reflux for 6 hr. The solution was then concentrated *in vacuo*, cooled, and poured into cold water. The semicrystalline precipitate was collected, washed, and dried to give 1.05 g. of **2**, m.p. 148–151° dec. A portion was recrystallized from ether to yield pure N-ethyl-17a-aza-D-homoandrost-4-en-3-one (**2**): m.p. 159–161°; ν_{max}^{KBr} 1660 (3-keto), 1625 (Δ^4) cm.$^{-1}$; n.m.r. 52.5 (18-CH_3), 60.0 (21-CH_3), 68.0 (19-CH_3), 3455. (C=CH of Δ^4) c.p.s.; $\lambda_{max}^{methanol}$ 237 mμ (log ϵ 4.09).

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Anal. Calcd. for $C_{21}H_{33}NO$: C, 79.94; H, 10.54; N, 4.44. Found: C, 79.62; H, 10.64; N, 4.66.

N-Hydroxy-17α-aza-D-homoandrost-4-en-3-one (4).—A solution of 900 mg. of N-ethyl-17a-aza-D-homoandrost-4-en-3-one (2) in 40 ml. of methylene chloride was cooled to 0–5°. To this, a solution of 700 mg. of 85% *m*-chloroperbenzoic acid in 30 ml. of methylene chloride was added slowly within a period of 10 min. The mixture was then allowed to stand for about 15 min. at room temperature, after which it was washed successively with a cold sodium carbonate solution and water and was dried over sodium sulfate. Removal of solvent yielded 950 mg. of oily N-oxide **3**, which was used without further purification.

The N-oxide **3** was dissolved in 30 ml. of xylene and heated under reflux in a nitrogen atmosphere for 20 min. The solvent was removed under reduced pressure and 850 mg. of an oily product was obtained which showed the presence of a hydroxyl band in the infrared. This oil in benzene solution was put on an alumina column. Elution of the column with benzene containing 50–75% ethyl acetate yielded identical fractions, m.p. 155–158°. These were combined to yield 600 mg. of N-hydroxy-17a-aza-D-homoandrost-4-en-3-one (**4**). A portion of this was recrystallized for analysis: m.p. 159–160°; ν_{max}^{KBr} 3200 (N–OH), 1660 (3-keto), 1625 (Δ^4) cm.$^{-1}$; n.m.r. 62.5 (C-18 CH_3), 70.5 (C-19 CH_3), 348.0 (C=CH of Δ^4) c.p.s.; $\lambda_{max}^{methanol}$ 237 mμ (log ε 4.08).

Anal. Calcd. for $C_{19}H_{29}NO_2$: C, 75.20; H, 9.63; N, 4.62. Found: C, 74.96; H, 9.70; N, 4.45.

N-Ethyl-17a-aza-D-homoestra-1,3,5(10)-triene-3-methyl Ether (6).—A solution of 1.8 g. of 3-methoxy-17a-aza-D-homoestra-1,3,5(10)-triene[12] (**5**) in 40 ml. of acetone was refluxed with 2 g. of diethyl sulfate and a solution of 2 g. of potassium hydroxide in 6 ml. of water for 4.5 hr. The solution was poured onto ice and the precipitated solids were filtered, washed, and dried to yield 1.6 g. of **6**, m.p. 100–103°. A portion of this was recrystallized from ether–hexane to give pure N-ethyl-17a-aza-D-homoestra-1,3,5(10)-triene-3-methyl ether (**6**): m.p. 104–105°; ν_{max}^{KBr} 1600 (C=C aromatic), 1560 (C=C aromatic), 1030 (O-CH_3) cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{31}NO$: C, 80.46; H, 9.97; N, 4.47. Found: C, 80.65; H, 9.96; N, 4.66.

N-Hydroxy-17a-aza-D-homoestra-1,3,5(10)-triene-3-methyl Ether (8).—A solution of 1.1 g. of the N-ethyl derivative **6** in 30 ml. of methylene chloride was cooled to 0–5° and a solution of 770 mg. of 85% *m*-chloroperbenzoic acid in 10 ml. of methylene chloride was added within a period of 10 min. The mixture was allowed to stand at room temperature for another 15 min. then was washed with cold solution of sodium carbonate and then water, and was dried over sodium sulfate. Removal of solvent yielded 1.15 g. of oily N-oxide **7**. This was dissolved in 50 ml. of toluene and heated under reflux in a nitrogen atmosphere for 15 min. Toluene was removed *in vacuo*, leaving 1.08 g. of a brown oil. The oil in benzene solution was put on an alumina column. Elution of the column with benzene containing 75–80% methylene chloride provided identical fractions, m.p. 140–142°. These were combined to yield 700 mg. of N-hydroxy-17a-aza-D-homoestra-1,3,5(10)-triene-3-methyl ether (**8**). A portion was recrystallized from ether for analysis: m.p. 143–145°; ν_{max}^{KBr} 3200 (N–OH), 1600 (C=C aromatic), 1560 (C=C, aromatic), 1030 (O-CH_3) cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.58; H, 9.00; N, 4.31.

The Decomposition of Spiranone *p*-Toluenesulfonylhydrazones. A Convenient Synthetic Route to Spirenes

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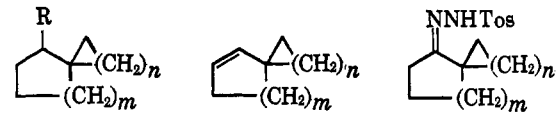
The dehydration of α-hydroxyspirans (**1**) to produce spirenes (**2**) is difficult to perform because of the tendency for carbon skeleton rearrangement to occur in these neopentyl-type systems.[2] In the dehydration of spiro[4.5]decan-6-ol (**1**, R = OH; $m = 2$; $n = 3$) over alumina about 50% of spiro[4.5]dec-6-ene (**2**, $m = 2$; $n = 3$) has been found along with the octalins resulting from ring expansion. The dehydration of this spiranol with sulfuric acid leads exclusively to octalins.[2b] The zinc chloride dehydrations of spiro[5.5]undecan-1-ol (**1**, R = OH; $m = 2$; $n = 4$) and spiro[4.5]decan-1-ol (**1**, R = OH; $m = 1$; $n = 4$) yield mainly cyclohexyl-1-cyclopentene *via* a ring contraction route[2d] and 1,2,3,4,5,6,7,8-octahydroazulene *via* a ring expansion route.[2f] The phosphoric acid dehydration of spiro[4.4]nonan-1-ol (**1**, R = OH; $m = 1$; $n = 3$) leads to 4,5,6,7-tetrahydroindane.[2d] The zinc chloride dehydration of the related system 2,2-dimethylcyclohexanol has been reported to yield olefins of rearranged carbon skeleton.[3] The products obtained from the acetolysis of α-tosyloxyspiranes (**1**, R = tosyl) are also predominantly rearranged olefins.[4]



1 **2** **3**

The basic decomposition of the *p*-toluenesulfonylhydrazones (tosylhydrazones, **3**) seemed to be potentially useful as a simple synthetic route to certain spirenes (**2**). The relative migratory aptitude of various ring sizes could also be determined and contrasted to the results of the products formed under ionic conditions.

The formation of olefins from the decomposition of tosylhydrazones was first investigated by Bamford and Stevens.[5] Friedman and Shechter have investigated the relationship between the products and the nature of the solvent in these decompositions (protonic or aprotic).[6] The decomposition of alkyl tosylhydrazones in aprotic solvents yields olefins *via* hydrogen migration and cyclopropanes *via* intramolecular insertion.[6b] The observation has been made that hydrogen migration occurs more readily than carbon skeleton rearrangement in the carbenoid decompositions. For example, the decomposition of the tosylhydrazone of pinacolone leads to *t*-butyl ethylene (52%) and 1,1,2-trimethylcyclopropane (47%). The decomposition of the tosylhydrazones of cyclopentanone and cyclohexanone yields cyclopentene and cyclohexene, respectively.[7] The tosylhydrazones of higher cycloalkanones produce intramolecular insertion products in addition to the cycloalkenes. In the decomposition of the tosylhydrazones of the C_7 through C_{10} ketones extensive 1,3-, 1,5- and 1,6-transannular insertion

(1) National Science Foundation Undergraduate Research Participant, 1963–1964.

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