chlorate: m.p. 206–208°; $\lambda_{max}^{CH_3CN}$, 240 mμ (log ε 4.64), 250 (4.56), 366 (4.12), 390 (3.92), 410 (3.88).

Anal. Calcd. for $C_{22}H_{18}ClNO_8$: C, 58.6; H, 3.8; Cl, 7.5; N, 3.0. Found: C, 58.3; H, 3.7; Cl, 7.5; N, 2.6.

4a,7a-Diazoniapentacene-6,13-dione Dibromide (20).—A mixture of 2,6-bis(bromomethyl)hydroquinone diacetate (**5**)[3] (169 g., 0.444 mole) and 2-(1,3-dioxolan-2-yl)pyridine (200 g., 1.32 moles) in 1 l. of acetonitrile was refluxed for 8 hr. and cooled to room temperature; the resulting salt **18** (251 g., 83%) was collected by filtration. Without further purification, 61.1 g. (0.09 mole) of it in 150 ml. of 48% hydrobromic acid was refluxed for 12 hr. and then refrigerated at 5° for 4 hr. The resulting crystals were filtered and recrystallized as yellow plates (21.0 g., 50%) from boiling water acidified with hydrobromic acid: $\lambda_{max}^{H_2O}$ 253 mμ (log ε 4.78), 383 mμ (log ε 4.36). The infrared spectrum exhibited a strong absorption at 5.95 μ.

Anal. Calcd. for $C_{20}H_{12}Br_2N_2O_2$: C, 50.9; H, 2.5; Br, 34.0. Found: C, 50.6; H, 2.3; Br, 33.8.

In a similar manner, **4a,11a-diazoniapentacene-6,13-dione (19)**[1] was obtained in 68% yield, starting with 2,5-bis(bromomethyl)hydroquinone diacetate.[3] It was recrystallized as lustrous yellow plates from boiling water containing a trace of hydrobromic acid. After drying at 140° over P_2O_5, the product existed as a monohydrate: λ_{max}^{MeOH} 224 mμ (log ε 4.66), 251 (4.70), 377 (4.41). The infrared spectrum exhibited a strong absorption at 5.95 μ.

Anal. Calcd. for $C_{20}H_{12}Br_2N_2O_2 \cdot H_2O$: C, 49.0; H, 2.9. Found: C, 49.0; H, 2.9.

6,7-Dihydroxy-4a,8a-diazoniapentaphene Dibromide (23).—A mixture of 3,6-bis(bromomethyl)catechol diacetate[3] (399 g., 1.05 moles) and 2-(1,3-dioxolan-2-yl)pyridine (400 g., 2.65 moles), in 750 ml. of acetonitrile was refluxed for 4 hr. The intermediary bis quaternary salt began to separate slowly as white needles as the viscous reaction mixture cooled to room temperature. Dilution with 2 l. of ether precipitated the remainder of the product as a semicrystalline mass. Recrystallization was effected by dissolving the product, with vigorous stirring, in 400 ml. of warm ethanol, which, in turn, was diluted with 1 l. of acetone and then ethyl acetate to incipient opalescence. The product **21** (522 g., 76%) slowly crystallized over a 12-hr. period at 5° and had m.p. 145–146°.

Anal. Calcd. for $C_{28}H_{30}Br_2N_2O_8 \cdot H_2O$: C, 48.1; H, 4.3. Found: C, 48.5; H, 4.5.

A mixture of a portion of the above product (36.4 g., 0.053 mole) and 200 ml. of 30% hydrogen bromide in acetic acid was refluxed for 45 min. Deep red crystals separated from solution during this period. After cooling, the mixture was diluted with 400 ml. of ether and the product was collected by filtration. Diazoniapentaphene (**23**) (21.2 g., 84%) was obtained as dark purple needles (hemihydrate) after recrystallization from boiling water containing 2 ml. of 48% hydrobromic acid, m.p. >450°. This material is not fluorescent and had λ_{max}^{MeOH} 229 mμ (log ε 4.51), 262 (4.42), 363 (4.61), 380 (4.60).

Anal. Calcd. for $C_2H_{14}Br_2N_2O_2 \cdot 0.5H_2O$: C, 49.6; H, 3.1. Found: C, 49.6; H, 3.0.

6,7-Diacetoxy-4a,8a-diazoniapentaphene bisperchlorate, m.p. 283° dec., was obtained as yellow needles by acetylation of **23** with acetic anhydride–sulfuric acid and then converting the product to the perchlorate salt. It is highly fluorescent in solutions of methanol, ethanol, or acetonitrile and had λ_{max}^{MeOH} 218 mμ (log ε 4.63), 253 (4.47), 300 (4.06), 345 (4.32), 360 (4.31), 367 (4.31), 386 (4.41).

Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_{12} \cdot 0.5H_2O$: C, 47.5; H, 3.1; Cl, 11.7. Found: C, 47.5; H, 3.2; Cl, 11.8.

7,8-Dihydroxy-5a-8a-diazoniaheptaphene Dibromide (24).—3-(1,3-Dioxolan-2-yl)isoquinoline, b.p. 127° (0.05 mm.), $n^{25}D$ 1.6055, was prepared from isoquinoline-3-carboxaldehyde[8] following the procedure used by Bradsher and Parham[7] for the synthesis of 2-(1,3-dioxolan-2-yl)pyridine.

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.6; H, 5.5; N, 7.0. Found: C, 71.5; H, 5.7; N, 7.1.

A mixture of 3,6-bis(bromomethyl)catechol diacetate[3] (22.8 g., 0.06 mole) and 3-(1,3-dioxolan-2-yl)isoquinoline (30 g., 0.15 mole) in 150 ml. of nitromethane was refluxed for 12 hr. The resulting quaternary salt was precipitated as a white powder by pouring the cooled solution into 500 ml. of ether. The product was collected and then a solution of it in 200 ml. of 48% hydrobromic acid was boiled for 30 min. A fine, bronze-colored crystalline material separated from solution during this period and was isolated by filtration. It was washed with ethanol and then ether, giving 19.0 g. (56%) of product, m.p. >450°. It was virtually insoluble in all of the common organic solvents and had $\lambda_{max}^{H_2O}$ 248 mμ (log ε 4.52), 269 (4.54), 300 (sh) (4.34), 419 (4.35), 440 (4.43).

Anal. Calcd. for $C_{28}H_{18}Br_2N_2O_2$: C, 58.6; H, 3.1; Br, 27.9; N, 4.9. Found: C, 58.5; H, 3.3; Br, 27.9; N, 4.9.

Acknowledgment.—The authors wish to thank Miss Jane O. Fournier for her assistance in some of the experimental work and Mr. D. G. Borden for providing the ultraviolet spectra.

(8) C. E. Teague and A. Roe, *J. Org Chem.*, **73**, 689 (1951).

Conformational Preferences in Malondialdehyde and Acetylacetaldehyde Enols Investigated by Nuclear Magnetic Resonance

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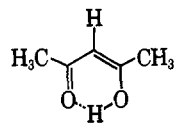
The spin–spin coupling constants obtained for the enol forms of malondialdehyde and acetylacetaldehyde indicate that the former is predominantly *sym-trans*, whereas the latter (and also the enol form of acetylacetone) is predominantly *sym-cis*. The conformational preferences of acrolein derivatives, therefore, depend on the existence and nature of substituents, and not solely on the possibilities for intramolecular hydrogen bonding. The n.m.r. parameters for *trans*-β-ethoxyacrolein are also presented.

Considerable space has been devoted in the literature to determinations of the conformation about the central C–C single bond in 1,3-butadiene and acrolein derivatives. In most cases, in the absence of constraints such as a bridging ring system, it has been shown that the stable form is planar *sym-trans*. There is considerable doubt as to whether the metastable form is planar *sym-cis* or nonplanar. In a few instances[2] it has been shown that either the *sym-cis* or the nonplanar conformation is actually more stable than the *sym-trans* form. One of the best known instances is the enol form of acetylacetone (I). In this case it is presumed that the planar *sym-cis* form is stabilized by the presence of an intramolecular hydrogen bond,[3] as in Ia. The n.m.r. spectrum obtained from such a compound, however, is the average of the spectra expected for Ia and b, since

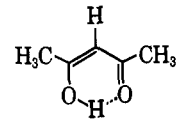
(1) Author to whom inquiries should be addressed.

(2) E. S. Waight and R. L. Erskine in "Steric Effects in Conjugated Systems," G. W. Gray, Ed., Butterworth and Co. (Publishers) Ltd., London, 1959; R. L. Erskine and E. S. Waight, *J. Chem. Soc.* 3425 (1960); G. J. Szasz and N. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953); H. Wynberg, A. de Groot, and D. W. Davies, *Tetrahedron Letters*, 1083 (1963).

(3) S. Bratoz, D. Hadzi, and G. Rossmy, *Trans. Faraday Soc.*, **52**, 464 (1956), and references therein.



Ia



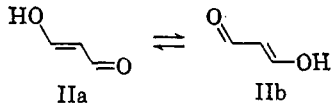
Ib

the tautomeric change (Whether this process is described in terms of resonance or of tautomerism depends upon the magnitude of the potential barrier between the two forms. Little is known about this barrier and we shall therefore, for convenience, use the tautomerism nomenclature.) is rapid compared with the n.m.r. time scale under normal conditions.[4] Thus, for instance, only a single peak due to the methyl protons is seen.

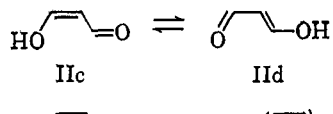
Other derivatives of acrolein which possess lability about the central C–C bond and yet prefer to be *sym-cis* or nonplanar rather than *sym-trans* are also ketones and not aldehydes.[2] Generally, too, these molecules have a substituent *cis* to the carbonyl group, as, for example, mesityl oxide. Infrared and ultraviolet spectroscopy have been extensively used to determine conformation for this type of compound, but so far n.m.r. techniques have been largely neglected. The present work was undertaken in conjunction with far infrared studies in an attempt to assess the importance of methyl substituents and of hydrogen bonding in deciding conformation in acrolein and butadiene derivatives. The far infrared investigations,[5] made entirely with compounds believed to be *sym-trans*, have shown that conjugated methyl ketones have *lower* barrier heights to internal rotation than the corresponding aldehydes. Since the presence of the methyl group is not expected to affect significantly the energy of the conformation of maximum energy, this is further proof that substitution of the aldehydic hydrogen by a methyl group destabilizes the *sym-trans* form.

Results and Discussion

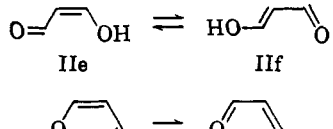
We have recorded and analyzed the proton n.m.r. spectra of the enol forms of malondialdehyde (II) and acetylacetaldehyde (III), as well as that of *trans*-β-ethoxyacrolein (*vide infra*). The parameters obtained for these substances in chloroform solution are given in Table I. It should be noted that the coupling constants for II and III are higher in aqueous solution, presumably owing to conformational changes. This



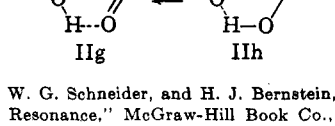
IIa IIb



IIc IId



IIe IIf



IIg IIh

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(5) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, in press.

TABLE I

PROTON N.M.R. PARAMETERS FOR ENOLS AND AN ENOL-ETHER IN CHLOROFORM SOLUTION

Compd.	Spectral type	Parameters
Malondialdehyde enol	AB_2	τ_A = 4.956 p.p.m.
		τ_B = 1.603 p.p.m.
		J_{AB} = 9.69 c.p.s.
Acetylacetaldehyde enol	ABX_3	τ_A = 4.403 p.p.m.
		τ_B = 2.097 p.p.m. (broadened)
		J_{AB} = 5.07 c.p.s.
		τ_X = 7.892 p.p.m.
		J_{AX}, J_{BX} < 1 c.p.s.
trans-β-Ethoxyacrolein	ABC	τ_A = 4.386 p.p.m.
		τ_B = 0.694 p.p.m.
		τ_C = 2.520 p.p.m.
		J_{AB} = 8.12 c.p.s.
		J_{AC} = 12.60 c.p.s.
		J_{BC} = <0.2 c.p.s.

observation will form the basis for further investigations. For II and III (as well as for I) there are actually four possible tautomeric pairs of isomers illustrated for II in IIa to h. These isomers are all interconvertible by the two processes of tautomerism and hindered internal rotation about a formal C–C single bond. It may be anticipated that both processes are sufficiently rapid that the n.m.r. spectrum is that for the weighted average of all possible forms (However, Forsén and Nilsson[6] assert that this is not true for analogous isomers of the enol form of the triketone 3-cinnamoylpentane-2,4-dione.). This implies magnetic equivalence of the terminal protons, so that an AB_2 spectrum is expected, and the long-range coupling constant, $J_{BB'}$, cannot be deduced from the spectrum.[4] It is likely that forms IId and f are relatively unstable with respect to c and e since the usual stability of *sym-trans* forms cannot be offset in this instance by intramolecular hydrogen bonding. It should be noted that we have not considered nonplanar conformations for similar reasons. Only *intermolecular* hydrogen bonding is possible for IIa–f.

Our principal interest has been the vicinal (H,H) coupling constant; owing to the averaging process there will be only a single observable value, J_{AB}. For the purposes of nomenclature, we regard each isomer as possessing alternating single and double bonds. We assume that we can represent the AB coupling constant in these forms with sufficient accuracy for the present purposes by a suitably weighted average of four characteristic coupling constants, J_c^s, J_t^s, J_c^d, and J_t^d. In each case the superscript s or d refers to vicinal coupling across a single bond or double bond, respectively, and the subscript t or c refers to a *trans* or *cis* arrangement of the coupled protons. Thus, in form IIa, one pair of protons is coupled with J_t^d, the other with J_t^s, and the value of J_t^s in IIa is assumed identical with that in IIb. These assumptions lead to eq. 1, following,

$$2\langle J_{AB}\rangle = p_{ab}(J_t^d + J_t^s) + p_{ce}(J_c^d + J_t^s) + p_{df}(J_c^s + J_t^d) + p_{gh}(J_c^d + J_c^s) \quad (1)$$

where p_{ab} is the total fractional population of forms IIa *and* b (themselves equally populated), etc.

We may estimate values of the four characteristic coupling constants as follows.

(6) S. Forsén and M. Nilsson, *Acta. Chem. Scand.* **14**, 1333 (1960).

J_c^d.—If it is assumed that substituent effects of an aldehyde group and an ethoxy group are additive, then from the *cis* coupling constants in ethylene (11.50 c.p.s.),[7] ethyl vinyl ether (6.95 c.p.s.),[8] and acrolein (10.00 c.p.s.)[9] one may calculate a value of 5.45 c.p.s. for the present case (neglecting differences between ethoxy and hydroxyl substituents). The value in γ-pyrone,[10] a reasonable model compound, is 5.9 c.p.s.

J_t^d.—Similarly, assuming additivity relations, but this time using the *trans* coupling constants in ethylene (19.0 c.p.s.),[7] ethyl vinyl ether (14.7 c.p.s.),[8] and acrolein (17.35 c.p.s.),[9] one obtains 13.05 c.p.s. for J_t^d. The validity of this type of treatment is checked by the fact that the observed value in *trans*-β-ethoxyacrolein (see below) is 12.60 c.p.s.

J_t^s—In unsubstituted and substituted acroleins which are largely in the *sym-trans* conformation, the coupling constant is near 8.0 c.p.s.; thus, acrolein, 7.81 c.p.s.[9]; *trans*-cinnamaldehyde, 7.7 c.p.s.[11]; *trans*-crotonaldehyde, 7.9 c.p.s.[12]; β-2-furylacrolein, 7.7 c.p.s.[13]; geranial, 7.73 c.p.s.[14]; neral, 7.95 c.p.s.[14]; and β-ethoxyacrolein, 8.1 c.p.s.

J_c^s.—The most questionable estimation is for this constant. One possible approach is to assume that the effect of a conformational change *sym-trans* → *sym-cis* is also additive with the substituent effects. Then the three values for butadiene (10.41 c.p.s.),[15] 1,3-cyclohexadiene (5.14 c.p.s.),[16] and *trans*-β-ethoxyacrolein (8.1 c.p.s.) lead to an estimation of $J_c^s \approx 2.8$ c.p.s. If the value for *trans*-1,4-diphenylbutadiene (10.8 c.p.s.)[14] be taken instead of that for butadiene itself, we find $J_c^s \approx$ 2.4 c.p.s. It should be emphasized that the geometry of cyclohexadiene may not be closely similar to that for the *sym-cis* molecules discussed here. In particular the diene fragment of cyclohexadiene is less likely to be planar than a six-membered ring containing a hydrogen bond.

We may, then, take average estimated values of J_t^d = 12.8 c.p.s., J_c^d = 5.7 c.p.s., J_t^s = 8.0 c.p.s., and J_c^s = 2.6 c.p.s. Substituting in eq. 1 and dividing by 2, one obtains the following.

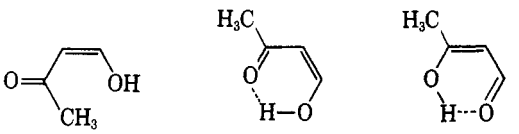
$$J_{AB}\ (\text{obsd.}) = 10.4p_{ab} + 6.85p_{ce} + 7.7p_{df} + 4.15p_{gh} \quad (2)$$

Now the measured value of J_{AB} is 9.69 c.p.s. As $\Sigma p = 1$, and no p can be negative, the minimum value p_{ab} can assume is obtained from the following equation.

$$9.69 = 10.4p_{ab} + 7.7p_{df}\ (\text{with } p_{ce} = p_{gh} = 0)$$
$$\text{where } p_{ab} \geq 0.74$$

Even this is low, since there is no reason to suppose that p_{df} would be appreciable compared with p_{ce}; *sym-trans* acrolein conformations are preferred in the absence of any special effect favoring it, such as intramolecular hydrogen bonding. If the assumption is made that $p_{df} = 0$, then $p_{ab} \geq 0.80$. The striking conclusion must be drawn that the tautomeric pair IIa ⇌ IIb predominates (that is, the molecule is *trans-sym-trans*) in contrast to the case for I. Some contributions from the other tautomeric pairs are presumably present, since J_{AB} is less than 10.4 c.p.s. However, the calculated values are only approximate; they are probably accurate to ±1 c.p.s.

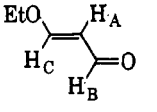
The enol form of acetylacetaldehyde obviously provides an intermediate case between I and II. Because of the loss of symmetry due to the substitution of a single methyl group, none of the isomers corresponding to IIa through h are equivalent. Consequently each one must be considered independently. The observed coupling constant for a $CDCl_3$ solution (see Experimental section) is 5.07 c.p.s. This is sufficiently close to J_c^d (calculated) that it is probable that either IIIa or b is predominant. Because of the known *sym-cis* form



IIIa IIIb IIIc

of I[3], we believe it is most likely that III exists under the conditions of the experiment mainly as IIIb, presumably with some admixture from c. The deduction that IIIb predominates over c is further strengthened by the chemical shift observed for the proton γ to the methyl group. The value τ 2.097 is closer to the corresponding ethylenic proton of *trans*-β-ethoxyacrolein (τ 2.520) than to the aldehydic proton (τ 0.694), whereas the value for the enol form of malondialdehyde (τ 1.603) is close to the average of the two *trans*-β-ethoxyacrolein values, as expected. This predominance of IIIb over c is, of course, in agreement with the statement made in the introduction that only ketones, not aldehydes, are known which prefer the *sym-cis* conformation. The fact that II is predominantly *sym-trans*, whereas both I and III are *sym-cis*, emphasizes the effect of replacing the aldehydic hydrogen by a more bulky group, specifically a methyl group.

For the above deductions use has been made of results from a study of the spectrum of β-ethoxyacrolein. Three groups of lines are observed. The assignment of the bands is straightforward, and yields coupling constants, 12.60 (vinylic) and 8.12 c.p.s. (aldehydic). The high value of the vinylic coupling constant indicates that the ethoxy and aldehyde groups are located *trans* to one another. As far as we are aware, this is the first time that the configuration of this product has been established. The value 12.60 c.p.s. for J_t^d is in good agreement with the calculated value used above for II and III. The value of the aldehydic coupling constant (8.12 c.p.s.) establishes that the conformation of the



IV

molecule is *sym-trans*, as expected (IV). We believe that this fact is probably a good indication that the corresponding hydroxy compound II prefers conformations

(7) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London) **A269**, 385 (1962); D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963); G. S. Reddy and J. H. Goldstein, *J. Mol. Spectry.*, **8**, 475 (1962).

(8) J. Feeney, A. Ledwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 2021 (1962); R. T. Hobgood, Jr., G. S. Reddy, and J. H. Goldstein, *J. Phys. Chem.*, **67**, 110 (1963).

(9) D. M. Grant and R. C. Hirst, private communication; A. W. Douglas and G. H. Goldstein, *J. Mol. Spectry.*, in press.

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(13) T. Schaefer, *Can. J. Chem.*, **40**, 1678 (1962).

(14) R. K. Harris and A. A. Bothner-By, unpublished work.

(15) R. T. Hobgood and G. H. Goldstein, *J. Mol. Spectry.*, **12**, 76 (1964).

(16) S. L. Manatt, private communication.

a and b rather than c or e, strengthening the deductions presented above for the predominance of forms IIa and b.

It is intended to make further detailed spectroscopic studies of these and closely related compounds in order to understand the conformational differences more fully.

Experimental

Solutions of II and III in $CDCl_3$ were obtained by hydrolysis of the acetals, $(EtO)_2CH \cdot CH_2CH(OEt)_2$ and $CH_3COCH(OMe)_2$, respectively, with an equal volume of dilute aqueous hydrochloric acid, followed by extraction with $CDCl_3$. The *trans*-β-ethoxyacrolein is obtained in small amount as a by-product of the hydrolysis of malondialdehyde tetraethyl acetal[17] and is preferentially extracted by the $CDCl_3$. A single n.m.r. tube was thus used to obtain the spectra of II and IV. This tube also contained a little ethanol, water, hydrochloric acid, and the original acetal. Similarly the $CDCl_3$ solution of III contained a little methanol, water, HCl, and the original acetal. In this case a small amount of the keto form (acetylacetaldehyde) could be detected. In both solutions only a single peak was observed for the protons of the water and hydrochloric acid together with the hydroxylic protons of the alcohol and the enol.

(17) L. A. Yanovskaya and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 667 (1962).

Acknowledgment.—We are grateful to Drs. G. M. Grant, R. C. Hirst, G. H. Goldstein, and A. W. Douglas for information on the n.m.r. parameters of acrolein in advance of publication. Similarly we are indebted to Dr. S. L. Manatt for the coupling constants in cyclohexadiene. Computation in this research was done with the support of the U. S. Air Force Office of Scientific Research under Grant AF-AFOSR 199-63.

Formation of 17α-Ethyl-17-methyl-8ξ,9ξ,13ξ,14ξ-gona-1,3,5(10)-trien-3-ol from 17α-Ethyl-19-nortestosterone. An Unusual Transformation

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The dehydration of 17α-ethyl-19-nortestosterone with pyridine hydrohalides yields two crystalline products, 17α-ethyl-17-methylgona-4,13-dien-3-one and 17α-ethyl-17-methyl-8ξ,9ξ,13ξ,14ξ-gona-1,3,5(10)-trien-3-ol. The latter structure was established by ultraviolet, infrared, and n.m.r. spectra and by dehydrogenation to 3′-ethyl-3′-methyl-1,2-cyclopentanophenanthrene.

In the presence of acids, a 17-hydroxy-17-alkyl steroid undergoes dehydration with concomittant migration of the angular methyl group (I to II). The resulting double bond has been shown to be at C-13 and C-14,[1] but, where there is additional unsaturation in the molecule, the double bond may migrate further to become part of an extended conjugated system. Thus, Kaufmann found that treatment of 17β-hydroxy-17-methylandrosta-1,4,6-trien-3-one with *p*-toluenesulfonic acid in acetic anhydride affords 1,17,17-trimethyl-13ξ,14ξ-gona-1,3,5(10),6,8-pentaen-3-ol acetate.[2]

As part of a study on the dehydration–rearrangement of the steroids carried out in these laboratories,[3] we found that treatment of 17α-ethyl-19-nortestosterone (III)[4] or the enol ether, 17α-ethyl-3-methoxyestra-2,5-(10)-dien-17-ol (IV),[4] with either pyridine hydrochloride or pyridine hydrobromide at 230–240° affords 17α-ethyl-17-methylgona-4,13-dien-3-one (V), a product which previously had been obtained from III with hydrogen chloride in acetic acid.[5] Besides V, we obtained yet another crystalline product, m.p. 152–153.5°, $[\alpha]D$ −17°, λ_{max} 279.5 mμ (ε 2220) and 286 mμ (ε 2100), from the reaction of either III or IV with the pyridine hydro halide.

The formation of this product, to which we assign the 17α-ethyl-17-methyl-8ξ,9ξ,13ξ,14ξ-gona-1,3,5(10)-trien-3-ol structure (VIa) is analogous to the transformation observed by Kaufmann.[2] The double bond that is generated by the removal of the hydroxyl group at C-17 migrates into conjugation with the unsaturated carbonyl group in ring A. Enolization then results in the aromatization of this ring. The presence of the phenolic hydroxyl group in VIa is supported by spectroscopic evidence and is confirmed by the formation of the methyl ether, VIb.

The n.m.r. spectra of both VIa and VIb show a signal at 57.5 c.p.s., which we attribute to the methyl group at C-17, as well as a pair of signals at *ca.* 51.5 and 48.5 c.p.s. Because the latter signals could not be unambiguously assigned to the methyl portion of the ethyl side chain, the possibility that the product was a D-homo steroid containing a pair of methyl group had to be considered.

In order to determine the size of ring D, VIa was dehydrogenated with palladium on charcoal between 210 and 285°.[2] In the process, elimination of the hydroxyl group also occurred, and 3′-ethyl-3′-methyl-1,2-cyclopentanophenanthrene (VII), m.p. 97–98.5°, $[\alpha]D$ −28.5, was obtained. The physical constants of this substance and the melting point of its trinitrobenzene complex are essentially identical with those of a product isolated from the selenium dehydrogenation of 3β-acetoxypregn-5-en-20-one, for which VII has been proposed as its most likely structure.[6]

The infrared and n.m.r. spectra of our sample of VII unequivocally establish its identity with that obtained

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