153–155°. The infrared spectrum of this material was identical to that of triphenylphosphine oxide.

**Procedure B.**—This procedure was used for Ib–e. A typical example follows. To a stirred solution of 6.5 g. (0.015 mole) of *p*-nitrobenzoylmethylenetriphenylphosphorane in 75 ml. of methylene chloride at *ca.* −30° was added 2.56 g. (0.016 mole) of percaprylic acid in 26 ml. of methylene chloride. The solution was stirred for 1.5 hr. and then concentrated *in vacuo* until crystallization occurred. Filtration afforded 1.14 g. (46%) of *p,p'*-dinitrodibenzoylethylene, m.p. 203–209°, which was recrystallized from methylene chloride, m.p. 208–211°.

*Anal.* Calcd. for $C_{16}H_{10}N_2O_6$: C, 58.99; H, 3.65. Found: C, 58.85; H, 3.21.

Similarly, Ib gave 57% of *p,p'*-dibromodibenzoylethylene, m.p. 189–191° (lit.,[21] 188.5°). The infrared spectrum was consistent with the assigned structure.

*p*-Acetamidobenzoylmethylenetriphenylphosphorane gave 43% of *p-p'*-diacetamidodibenzoylethylene, m.p. 282–284°.

*Anal.* Calcd. for $C_{20}H_{18}N_2O_4$: C, 68.60; H, 5.14. Found: C, 68.37; H, 5.46.

*p*-Methoxybenzoylmethylenetriphenylphosphorane gave 57% of *p-p'*-dimethoxydibenzoylethylene, m.p. 165–167°.

*Anal.* Calcd. for $C_{18}H_{16}O_4$: C, 73.00; H, 5.42. Found: 73.53; H, 5.61.

**Reaction of I and Phenylglyoxal.**—To a stirred solution of 10.0 g. (0.0262 mole) of I in 200 ml. of dry benzene was added dropwise at room temperature 3.5 g. (0.0262 mole) of phenylglyoxal in 150 ml. of dry benzene. Immediately after the addition an aliquot was titrated.[15] It was found that 98% of I had reacted. Evaporation of a portion of the benzene afforded a solid whose infrared spectrum had all of the bands of *trans*-1,2-dibenzoylethylene. The bulk of the solution was evaporated to give a yellow solid which was recrystallized from absolute ethanol to give *trans*-1,2-dibenzoylethylene, m.p. 110–111°.

**Addition of I to Peracetic Acid.**—Several experiments were conducted in which I (1 mole) was added to peracetic acid (2 moles). All other conditions were maintained as close as possible to those used for the dimer-forming reaction. In all cases it was possible to isolate good yields of triphenylphosphine oxide. In no case was *trans*-1,2-dibenzoylethylene isolated. Small amounts of neutral oils were obtained.

To make sure that the excess peracid was not decomposing the *trans*-1,2-dibenzoylethylene, a control experiment was conducted. Treatment of 1.0 g. (0.00424 mole) of crude *trans*-1,2-dibenzoylethylene, m.p. 98–108°, which was obtained from a dimerization reaction, with 0.88 ml. (0.004 mole) of 40% peracetic acid for 17 hr. in 25 ml. of benzene gave, after extraction with base and water and evaporation of the solvent, 1.0 g. of *trans*-1,2-dibenzoylethylene, m.p. 98–108°. There was no depression on admixture with the starting material. The infrared spectra of the two compounds were identical.

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[21] J. B. Conant and R. Lutz, *J. Am. Chem. Soc.*, **47**, 891 (1925).

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# Conformational Analysis. XXXV. The Configurations and Conformations of Ring A in the 2-Fluoro-5α-Androstane-3,17-Diones[1,2]

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The dipole moments, rotatory dispersions, ultraviolet, infrared, and proton magnetic resonance spectra of 2α- and 2β-fluoroandrostane-3,17-dione have been determined and prove that the previously assigned configurations are correct. Ring A is in the chair conformation in both compounds.

Recent interest in compounds containing a fluorine atom on a carbon adjacent to a carbonyl group[4–7] prompted us to study further the 2-fluoro-3-keto steroids. The only compounds of this type so far reported for which both of the C-2 epimers are known are the 2-fluoroandrostane-3,17-diones[8] and related C-17 oxygenated compounds. There are a variety of physical methods which have been and may be used to establish the configuration of the halogen in such compounds, and these include infrared spectra,[7,9] ultraviolet spectra,[7,10] rotatory dispersion,[11] nuclear magnetic resonance spectra,[12] polarographic reduction potentials[13] and dipole moments.[7,14] Of these, the latter is one of the more definitive and has been used in the present work. The problem is more difficult than other similar cases which have been studied,[4–7] because the oxygen at C-17 introduces an extra unwanted dipole into the system. If the oxygen is as a hydroxyl or acetoxyl, conformational ambiguities exist, but this difficulty is alleviated by studying the 17-ketones which are also known compounds.

The two known epimers of 2-fluoro-5α-androstane-3,17-dione have had their configurations assigned previously on the basis of their methods of preparation and their spectral properties.[8] The aims of the present investigation were to confirm the configurational assignments, to examine the conformation of ring A in these compounds, and to develop general methods for dealing with molecules containing more than two dipoles.

Assuming initially an ordinary regular chair conformation for ring A, the moments expected for the 2α- and the 2β-fluoroandrostane-3,17-diones were calculated. The necessary data were obtained by projecting a Dreiding model of the molecule into a coördinate

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[1] Paper XXXIV, N. L. Allinger, J. Allinger, M. A. DaRooge, and S. Greenberg, *J. Org. Chem.*, **27**, 4603 (1962).

[2] This research was supported in part by the U. S. Army Research Office under grant number DA-20-018-ORD 22743, and in part by the National Science Foundation under grant number 19981.

[3] Predoctoral U. S. Public Health Service Fellow, General Division of Medical Sciences, 1960–1962.

[4] N. L. Allinger, H. M. Blatter, M. A. DaRooge, and L. A. Freiberg, *J. Org. Chem.*, **26**, 2550 (1961).

[5] (a) A. H. Nathan, B. J. Magerlein, and J. A. Hogg, *J. Org. Chem.*, **24**, 1517 (1959); (b) H. M. Kissman, A. M. Small, and M. J. Weiss, *J. Am. Chem. Soc.*, **82**, 2312 (1960); (c) J. S. Mills, A. Bowers, C. Djerassi, and H. J. Ringold, *ibid.*, **82**, 3399 (1960); (d) J. Edwards and H. J. Ringold, *ibid.*, **81**, 5262 (1959); (e) A. H. Nathan, J. C. Babcock, and J. A. Hogg, *J. Org. Chem.*, **24**, 1395 (1959); (f) R. B. Gabbard and E. V. Jensen, *ibid.*, **23**, 1406 (1958).

[6] N. L. Allinger, M. A. DaRooge, and C. L. Neumann, *ibid.*, **27**, 1082 (1962).

[7] N. L. Allinger and H. M. Blatter, *ibid.*, **27**, 1523 (1962).

[8] P. D. Klimstra and R. E. Counsell, *J. Med. Pharm. Chem.*, **5**, 1216 (1962).

[9] R. N. Jones, D. A. Ramsey, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952).

[10] R. C. Cookson, *J. Chem. Soc.*, 282 (1954).

[11] C. Djerassi, "Optical Rotatory Dispersion: Applications to Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1960, p. 115.

[12] E. J. Corey, private communication.

[13] A. M. Wilson and N. L. Allinger, *J. Am. Chem. Soc.*, **83**, 1999 (1961).

[14] A. S. Kende, *Tetrahedron Letters*, **14**, 13 (1959).

system and measuring the coordinates of the atoms at each end of each dipole. From the coördinates, knowing the magnitude of each individual dipole, to calculate the resultant of three dipoles is in general a straightforward but somewhat tedious task, and therefore a program was written for the IBM 650 computer which would do these calculations accurately in quite a general way. The details of the method of calculation are described in the appendix.

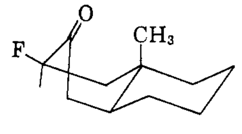
Because of the relatively high polarizability of the carbonyl oxygen ($0.84 \times 10^{-24}$ cm.$^3$),[15] the moment induced in the C=O group by the neighboring equatorial C—F dipole must be taken into account. The value 3.01 (from cholestan-3-one)[4] was consequently used for the C=O dipole when the fluorine was axial, and 2.84 D. was used when it was equatorial.[16] Since the polarizability of the fluorine ($0.38 \times 10^{-24}$ cm.$^3$)[15] is almost the same as that of hydrogen ($0.42 \times 10^{-24}$ cm.$^3$),[15] the same value for the C—F bond moment, 1.94 D.,[6] was used throughout the calculations. Similarly the value 2.98 D. was used throughout for the C-17 carbonyl.[18] The dipole moment of 2α-fluoroandrostane-3,17-dione was thus calculated to be 4.68 D, and that of 2β-fluoroandrostane-3,17-dione (chair form) was calculated to be 2.44 D.

The dipole moment of the presumed 2α-fluoroandrostane-3,17-dione was measured in benzene solution, and the value found was 4.69 D. The configuration at C-2 was therefore confirmed in an unequivocal manner.

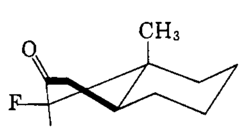
The moment of the compound believed to be 2β-fluoroandrostane-3,17-dione was determined in benzene solution, and an experimental value of 3.15 D. was found. While this value supports unequivocally the configuration previously assigned, it did appear to be larger than the calculated value by more than experimental error.

There are at least two different reasonable physical situations which might lead to the result observed with the β-fluoro compound. Either the molecule is deformed in such a way as to increase its moment, or it exists as an equilibrium mixture of two (or more) forms. The deviation from a simple perfect chair which was observed doubtlessly arises primarily from the repulsion which occurs between the C-19 methyl and the axial fluorine. A van der Waals calculation[19] gives this energy as 4.8 kcal./mole, and certainly this would be sufficient to bring about a deformation of some sort. An examination of models shows that a deformation which pushes apart the fluorine and the 19-methyl by flattening out the ring somewhat is possible, and rough calculations of energetics can be made. If the C—F bond is bent away from the methyl by 10°, the repulsion is decreased to about 1.0 kcal./mole, but at the expense of about 1.7 kcal./mole in bending energy. The total energy of this bent structure is then roughly 2.7 kcal./mole, an improvement of about 2.1 kcal. over that of the regular chair. Such a distortion seems therefore a reasonable possibility, and it would increase the dipole moment to a value to within experimental error of that observed.

The other way in which the molecule might attempt to relieve the repulsion present in the regular chair would be to go over to the flexible form (I or II). Models show that I is unfavorable because of the methyl–carbonyl repulsion, while II does not suffer from such an interaction. Further, only one eclipsed ethane exists in II, as opposed to two in I. Hence conformational considerations indicate that the probable structures for the 2β-fluoro-3-ketone are the deformed chair and II.[21] Williamson and Johnson[22] have presented proton magnetic resonance data on 2β-acetoxycholestan-3-one which they have interpreted as indicative of a ring A structure similar to II. Since oxygen and fluorine are quite similar in size, there would appear to be an analogy for II.



I



II

The dipole moments for I and II were calculated from measurements on Dreiding models as before, and the values obtained were 4.7 and 4.3 D., respectively. If I is eliminated as a possible structure on the basis of steric considerations, the moment of the actual compound in benzene solution shows that it exists largely as a (deformed) chair, but a sizeable amount of II may be present. If II is present to any substantial degree, then increasing the polarity of the solvent should shift the equilibrium toward II, since the larger dipole is stabilized more by an increase in the effective dielectric constant of the medium.[23] The available material was not sufficient to permit determination of the dipole moment in another solvent, however. Spectroscopic studies were, therefore, undertaken to try to ascertain whether or not any detectable amount of II actually was present. These studies were of rotatory dispersion, ultraviolet, infrared, and n.m.r. spectra.

It is known[7,8,24] that an equatorial fluorine adjacent to the carbonyl causes little or no shift in the ultraviolet spectrum relative to the parent, while an axial fluorine does cause an increase in the wave length of maximum absorption by 10–18 mμ. With these diones the spectrum observed is the resultant of the 3- and 17-ketones, and to examine the former, the latter must be subtracted from the observed spectrum. The spectra of 17-androsterone, androstane-3,17-dione and the 2α- and 2β-fluoroandrostane-3,17-diones were therefore determined in solvents of varying polarity. The spectrum of the 17-ketone was subtracted from

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(15) J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co. New York, N. Y., 1958, p. 91.

(16) The latter value was arrived at by assuming the moment induced in the carbonyl by the C—F dipole had the same magnitude as that induced in a carbonyl group by a C—Br dipole. The value in the case of the C—Br dipole was known experimentally.[17]

(17) W. D. Kumler and A. C. Huitric, *J. Am. Chem. Soc.*, **78**, 3369 (1956).

(18) N. L. Allinger and M. A. DaRooge, *ibid.*, **84**, 4561 (1962).

(19) The method of Hill (ref. 20) was used for this calculation. See ref. 6 for the pertinent numerical data.

(20) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

(21) Actually I and II are extremes of the flexible form. The geometry of this form which is of minimum energy may not be exactly II, but may be between I and II.

(22) K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 4623 (1961).

(23) J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958).

(24) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960, p. 115.

that of each dione in the corresponding solvent. The remaining spectra, (of the 3-ketones alone) are given in Table I, and are consistent with the fluorine being axial in the 2β isomer and equatorial in the 2α. No shift of equilibrium could be detected by this method.

TABLE I

ULTRAVIOLET SPECTRA OF THE 3-KETONE GROUP OF THE ANDROSTANE-3,17-DIONES[a]

| | Abs. ethanol | | Dioxane | | Chloroform[b] | |
|---|---|---|---|---|---|---|
| Solvent | $\lambda_{max}$ | $\epsilon$ | $\lambda_{max}$ | $\epsilon$ | $\lambda_{max}$ | $\epsilon$ |
| 3,17-dione | 283 | 21 | 291 | 17 | 293 | 15 |
| 2αF- | 285 | 37 | 291 | 40 | 293 | 37 |
| 2βF- | 293 | 23 | 298 | 25 | 301 | 28 |

[a] Calculated values (see text). [b] Alcohol free solvent.

It may be noted that the shifts observed of the $\lambda_{max}$ in the ultraviolet spectra of numerous 2-axial fluoro ketones (relative to the unfluorinated parents) vary from 10 to 18 mμ in cases where there is no other syn axial substituent. In this case the shifts are smaller, 7 to 10 mμ. If the fluorine is bent down toward the plane of the carbonyl, theory predicts just such a shift.[25]

The carbonyl stretching frequencies of the 3- and 17-ketones in the infrared could not be resolved with the available spectrometers and were hence of no use for conformational studies.

The infrared spectrum of the 2α isomer in chloroform showed a characteristic fingerprint consisting of five strong bands of nearly equal intensity at 9.03, 9.20, 9.45, 9.67, and 9.91 μ in chloroform solution. The spectrum was essentially unchanged when determined in a Nujol mull. When the spectrum of the 2β isomer was determined in Nujol, it was found to be essentially the same as that of the 2α isomer in this region. The spectrum of the 2β isomer in chloroform on the other hand was totally different in this region (medium band at 9.03, strong band at 9.88 and very weak bands at 9.48, 9.57, and 9.70 μ).

The most reasonable interpretation of the infrared data would seem to be that with the 2β isomer there is a drastic conformational change in the molecule in going from the crystal (mull) to chloroform solution. The structure in solution seems to be certainly that of a chair, so it seems quite likely that in the crystal ring A is in fact in the flexible form.

The proton magnetic resonance spectra were determined for both the 2α and the 2β isomers in a polar solvent (acetonitrile) and in a nonpolar solvent (chloroform).[26] The 2α isomer (in chloroform) gave a pair of quartets of the ABCX type in the region appropriate for the proton at C-2, with coupling constants of 7, 12, and 50 c.p.s. These coupling constants are reasonably consistent with *gauche* and *trans* hydrogen, and geminal fluorine respectively. The 2β isomer (in chloroform) gave a pair of triplets of the $AB_2X$ type, with coupling constants of 4 and 49 c.p.s. This means that the coupling constants are the same between the proton at C-2 and each proton at C-1. The magnitude of this coupling constant is reasonable for a *gauche* arrangement and is quite consistent with an ordinary or slightly deformed chair. It would appear that the *gauche* coupling constant is larger than that advocated for the corresponding acetoxy compounds.[22] There was little change in the coupling constants when the solvent was changed to acetonitrile.[27] The data are summarized in Table II.

TABLE II

PROTON MAGNETIC RESONANCE DATA FOR 2α- AND 2β-FLUOROANDROSTANE-3,17-DIONES[a]

| | Deuteriochloroform | | | | Acetonitrile | | | |
|---|---|---|---|---|---|---|---|---|
| | | $J_{Ha}$ | $J_{He}$ | $J_{HF}$ | | $J_{Ha}$ | $J_{He}$ | $J_{HF}$ |
| 2α-F | 5.02 | 12.4 | 7.0 | 49.7 | 3.92 | 12.7 | 7.4 | 47.7 |
| 2β-F | 5.24 | 3.9 | 3.9 | 49.3 | 5.09 | 6.1 | 6.1 | 49.5 |

[a] Coupling constants accurate to about ±0.1 c.p.s.

The rotatory dispersion curve of the β isomer was determined in absolute ethanol and in chloroform solution. The curve showed no significant change with changing solvent. While the sign of the Cotton effect would be negative for I, it is not now possible to predict with confidence even the sign of the curve for II. However, the fact that the observed curve is positive and invariant is, consistent with, but does not prove, that ring A is in the chair form. The amplitude of the curve ([A] = +152) was less positive than that of the 2α isomer ([A] = +198). If ring A is deformed slightly [A] becomes less positive,[18] and similarly the smaller atomic refraction of fluorine relative to hydrogen causes a further decrease, and the observed results are as expected.

The conclusions consistent with all the data for the compounds in solution are as follows: (1) The previously assigned configurations are correct; (2) Both the 2α- and the 2β-fluoro-3-ketones have ring A in a chair form; (3) There is no evidence for any boat form in equilibrium with the chair, but the possibility of the presence of a few per cent cannot be excluded.

## Experimental

**2α-Fluoroandrostane-3,17-dione.**—The compound was used as received, needles, m.p. 208–210°. The ultraviolet spectrum was determined in ethanol ($\lambda_{max}$ 285, $\epsilon$ 37), chloroform ($\lambda_{max}$ 293, $\epsilon$ 37) and dioxane ($\lambda_{max}$ 291, $\epsilon$ 40). The infrared spectrum showed a strong unresolved doublet carbonyl band at 5.74, 5.78 μ ($CHCl_3$), and the spectrum in a Nujol mull was qualitatively the same as in chloroform. The proton magnetic resonance spectrum was determined in deuterochloroform and in acetonitrile, and the results are summarized in Table II. The rotatory dispersion curve was measured in absolute ethanol (*c* 0.0427): $[\alpha]_{700}$ + 4.3°, $[\alpha]_{589}$ +0°, $[\alpha]_{313}$ + 3157°, $[\alpha]_{274}$ −3337°.

**2β-Fluoroandrostane-3,17-dione.**—This compound was received as two samples, the sample used for the dipole moment work, needles, had m.p. 140–143°, while the other sample used for the spectroscopic studies had m.p. 142–145°, and was shown by the proton magnetic resonance spectrum to contain about 5% impurity which showed vinyl hydrogen, and which was probably the $\Delta^2$ compound formed by elimination. The ultraviolet spectrum was determined in ethanol ($\lambda_{max}$ 293, $\epsilon$ 23), chloroform ($\lambda_{max}$ 301, $\epsilon$ 28) and dioxane ($\lambda_{max}$ 298, $\epsilon$ 25). The infrared spectrum showed a strong carbonyl band at 5.75 μ ($CHCl_3$), and the spectrum in a Nujol mull was qualitatively quite different from that in chloroform. The proton magnetic resonance spectrum was determined in deuterochloroform and in acetonitrile, and the results are summarized in Table II. The rotatory dispersion curve was measured in two solvents; in chloroform (*c* 0.036): $[\alpha]_{600}$ +99°, $[\alpha]_{400}$ +388°, $[\alpha]_{317}$ +2719°, $[\alpha]_{300}$ +884°; in

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(25) (a) A. Julg, *J. Chim. phys.*, 453 (1956); (b) M. A. Miller and R. B. Hermann, unpublished results.

(26) The effective polarities of these solvents as far as the equilibria of 2-halocyclohexanones are concerned have been shown previously (see ref. 23 and 27).

(27) This solvent is known to be highly polar with regard to equilibria of α-halo ketones (B. Waegell, theses, Universite de Strasbourg, 1961; also see E. M. Kosower, G. Wu, and T. S. Sorensen, *J. Am. Chem. Soc.*, **83**, 3147 (1961)).

absolute ethanol ($c$ 0.039): $[\alpha]_{600}$ $+54°$, $[\alpha]_{400}$ $+354°$, $[\alpha]_{315}$ $+2695°$, $[\alpha]_{275}$ $-2269°$, $[\alpha]_{260}$ $-1710°$.

**Dipole Moments.**—The dipole moment instrument used has been described earlier.[4] The dipole moments were measured in benzene and dioxane solutions and the calculations were carried out essentially by the method of Halverstadt and Kumler[28] utilizing an IBM 650 computer programmed as described earlier.[29] Atomic polarization has been taken into account approximately by setting it equal to 10% of the molar refractivity. The latter was calculated from Tables.[30] The data are summarized in Table III.

TABLE III

DIPOLE MOMENTS
(Benzene solution, 25°C.)

| $N_2$ | $d_{12}$ | $\epsilon_{12}$ |
|---|---|---|
| 2β-Fluoroandrostane-3,17-dione—$M_R$ 89.36 cc. | | |
| 0.00000000 | 0.873502 | 2.2752 |
| 0.00020643 | 0.873727 | 2.2784 |
| 0.00043190 | 0.873941 | 2.2816 |
| 0.00126987 | 0.874711 | 2.2941 |
| 0.00196165 | 0.875243 | 2.3039 |
| $\alpha = 14.653$ | $\epsilon_1 = 2.2753$ | $d_1 = 0.87354$ |
| $\beta = 0.889$ | $P_{2\infty} = 292.5$ | $\mu = 3.15 \pm 0.02$ D. |
| 2α-Fluoroandrostane-3,17-dione | | |
| 0.00000000 | 0.873562 | 2.2760 |
| 0.000299878 | 0.873797 | 2.2855 |
| 0.000407469 | 0.873870 | 2.2890 |
| 0.000593583 | 0.874124 | 2.2947 |
| 0.000724309 | 0.874211 | |
| $\alpha = 31.506$ | $\epsilon_1 = 2.2761$ | $d_1 = 0.87353$ |
| $\beta = 0.940$ | $P_{2\infty} = 538.2$ | $\mu = 4.69 \pm 0.10$ D. |

## Appendix

**Calculation of the Resultant Dipole Moment from Any Number of Separate Group Moments.**—The individual dipoles are vectors ($v_i$), the magnitudes of which are the group moments, and the directions of which are given by the coordinates of the atom at the negative end of the dipole minus the coördinates of the atom at the positive end, $(x_i, y_i, z_i) = (\Delta x, \Delta y, \Delta z)$, these being the quantities available from the measurements on the models. The bond length ($L_i$) of the group dipole is:

$$L_i = (x_i^2 + y_i^2 + z_i^2)^{1/2}$$

and this length is related to the group moment ($\mu_i$) by

$$\mu_i = k_i L_i$$

For each $v_i$, $k_i$ must be calculated. The projections of $v_i$ on the axes then are:

$$v_i = (k_i x_i, k_i y_i, k_i z_i)$$

The resultant moment is given by

$$\mu = [(\sum_i k_i x_i)^2 + (\sum_i k_i y_i)^2 + (\sum_i k_i z_i)^2]^{1/2}$$

As a check on the accuracy of the measurement of the coördinates of the various atoms, the resultant moment was then recalculated as above, except that instead of calculating $L_i$ from the coördinates it was given the computer as input, since this quantity is known to be just the bond length between the atoms which make up $v_i$. The value of $\mu$ obtained here was then compared with the value obtained by the previous method. A variation of more than about 0.05 D. for each vector (or of more than 0.15 D. in the present cases) between the moments calculated by the two methods indicated that the coördinates had not been measured with sufficient accuracy.

An IBM 650 program was written with the aid of a GATE compiler which took as input five quantities for each vector ($x_i$, $y_i$, $z_i$, $L_i$, $\mu_i$), carried out the calculation, and gave as output two values of the resultant ($\mu$) calculated as outlined. Taking the various sources of error into account, it is felt that the resultant moments calculated are accurate to 0.1 D. per vector (0.3 D. in the present cases) or better.

**Acknowledgment.**—The authors are indebted to Dr. P. D. Klimstra of G. D. Searle and Co., Chicago, for furnishing them with samples of the 2-fluoroandrostane-3,17-diones, to C. L. Neumann for measuring some of the dipole moments, and to Dr. Merle Emerson for the proton magnetic resonance spectra and helpful discussion regarding them.

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[28] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[29] N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

[30] A. I. Vogel, W. T. Cresswell, G. J. Jeffrey, and J. Leicester, *Chem. Ind.* (London), 358 (1950).

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# An Aromatization Reaction of a Cross-conjugated Dienone System with Zinc. II. Aromatization of Steroidal 1,4-Dien-3-one and 1,4,6-Trien-3-one System with Zinc[1]

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Treatment of androsta-1,4-diene-3,17-dione, androsta-1,4-diene-3,11,17-trione, and androsta-1,4,6-triene-3,17-dione with zinc in pyridine gave rise to the corresponding $p$-cresol type of rearrangement product, a 9,10-seco derivative and 6-dehydroestrone, respectively. When acetic acid was used as a solvent in this reaction, these cross-conjugated dienone or trienone derivatives were converted to the polyenic bissteroids.

In a previous communication,[2] we described a new type of dienone–phenol rearrangement of cross-conjugated dienone or trienone systems, involving aromatization of ring A with concomitant elimination of the C-19 angular methyl group.

In 1953, Barton and Thomas[3] reported the rearrangement of 3β-acetoxylanosta-5,8-dien-7-one with zinc in acetic acid to a phenolic substance, whose structure

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[1] This paper constitutes Part XXXVII of a series entitled "Steroid Studies" by K. Tsuda.

[2] K. Tsuda, E. Ohki, S. Nozoe, and N. Ikekawa, *J. Org. Chem.*, **26**, 2614 (1961).

[3] D. H. R. Barton and B. R. Thomas, *J. Chem. Soc.*, 1842 (1953).