utilized the reaction between Δ^5-3β-acetoxyetiocholenyl chloride and dimethylcadmium to introduce the 20-keto-21-methyl group. The course of this reaction is sensitive to changes in reagent concentration, and Δ^5-3β-acetoxyetiocholenic acid methyl ester may be obtained instead of the desired Δ^5-pregnenol-3β-one-20-acetate. These two compounds possess identical melting points and optical rotations, and show no mixed melting point depression. The required 20-ketone absorbs at 1706 cm.$^{-1}$ and the undesired methyl ester at 1735 cm.$^{-1}$ so that measurement of the carbonyl region of the infrared spectrum provided a rapid method for the identification of the product.

Concluding Remarks

For convenience in presentation, the infrared absorption characteristic of the side chain structures have been treated here independently of absorption within the ring system. This separation is of course an artificial one, and in the evaluation of the infrared absorption of any individual compound the absorption of the whole molecule must be considered, as was done in the case of XXXIX above.

Acknowledgments.—The authors wish to thank the several investigators listed individually in a footnote to Table I, who kindly made available many of the compounds. The technical assistance of Mr. D. S. Keir and Mr. R. Lauzon at the National Research Council and Miss B. Boland and Miss R. Connolly at the Sloan–Kettering Institute is also gratefully acknowledged.

This investigation was aided by grants from the American Cancer Society (upon recommendation of the Committee on Growth of the (U. S.) National Research Council), the Commonwealth Fund, the Anna Fuller Fund, the Albert and Mary Lasker Foundation, the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL OF CANADA[1] AND THE SLOAN-KETTERING INSTITUTE FOR CANCER RESEARCH]

The Infrared Spectra of α-Brominated Ketosteroids

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The effect of bromination at the α-carbon atom on the carbonyl stretching bands in the infrared spectra of keto steroids is shown to depend on the stereochemical configuration of the carbon–bromine bond. It is suggested that if the bromine atom enters at an equatorial position on the cyclohexanone ring, in the chair configuration the band is displaced by about 20 cm.$^{-1}$ to higher frequency while bromination at a polar position causes little displacement. The 20-ketone band is similarly displaced by about 20 cm.$^{-1}$ on bromination at C-21 but is hardly affected by bromination at the 17α-position. A diminution in the integrated adsorption intensity accompanies a positive frequency shift on bromination. These observations aid in the determination of the steric configuration and structure of brominated ketosteroids.

In the course of a systematic study of the infrared spectra of steroids, it has been observed that, in certain instances, the spectra may be influenced in a characteristic manner by stereochemical as well as by structural differences. One example of such stereochemical specificity involving the C–O stretching vibrations at 1200–1250 cm.$^{-1}$ in the spectra of 3α- and 3β-acetoxy steroids has been discussed previously.[2] The frequency[3] and intensity[4] of the carbonyl stretching bands in ketosteroids are influenced by bromination at an adjacent methylene group, and it is the purpose of this communication to show that the effect of such α-bromination depends on the stereochemical configuration of the carbon–bromine bond.

Experimental Methods and Results

The spectra were determined on a Perkin-Elmer Model 12C spectrometer, using a calcium fluoride prism. The frequencies of the carbonyl maxima, which are given in Table I, were determined after correction for water vapor and solvent absorption, and the estimated accuracy is ±1 cm.$^{-1}$. A few of the measurements, indicated in the table by an asterisk, were made with a sodium chloride prism; these are accurate to ±3 cm.$^{-1}$. The integrated absorption intensities were determined by the modification of the Wilson and Wells method described previously[4] for polycarbonyl compounds.

Discussion

In the *3-ketones*, the introduction of a single α-bromine atom increases the frequency of the carbonyl maximum by 13–19 cm.$^{-1}$ and depresses the integrated absorption intensity[4] by about 25%. The introduction of a second bromine atom at *the same α-carbon atom* to form a gem dibromide produces little further change in either the carbonyl frequency or intensity, but if a second bromine atom is introduced on the α'-methylene group, to yield a 2,4-dibromo-3-ketone, an additional increase of about 20 cm.$^{-1}$ occurs in the carbonyl frequency and the intensity is further depressed. A positive frequency shift is observed also in a *6-bromo-7-ketone* (see Table I). In some of these compounds, *e.g.*, 2-bromoandrostanol-17-one-3-hexahydrobenzoate, the brominated carbonyl band overlaps ester carbonyl absorption at 1735–1740 cm.$^{-1}$.

In the *11-bromo-12-ketones* series, the two com-

(1) Published as Contribution No. 2696 from the Laboratories of The National Research Council of Canada, and No. XIII in the series "Studies in Steroid Metabolism."

(1a) Died March 10, 1952.

(2) R. N. Jones, P. Humphries, F. Herling and K. Dobriner, THIS JOURNAL, **73**, 3215 (1951).

(3) R. N. Jones, P. Humphries and K. Dobriner, *ibid.*, **72**, 956 (1950).

(4) R. N. Jones, D. A. Ramsay, D. S. Keir and K. Dobriner, *ibid.*, **74**, 80 (1952).

TABLE I

CARBONYL BAND POSITIONS AND POSTULATED STERIC CONFIGURATIONS FOR BROMINATED KETOSTEROIDS

Compound[a]	Carbonyl position, cm.$^{-1}$	Band[b] intensity	Frequency shift on bromination	Conformation of C–Br bond	Configuration of C–Br bond
3-Ketones					
Cholestanone-3	1718	2.62	..	..	.....
2-Iodocholestanone-3	1724	2.00	6[c]	[e]	α
2-Bromocholestanone-3	1733	1.93	15	[e]	α
2,2-Dibromocholestanone-3	1735	1.83	17	[e,p]	α,β
2,4-Dibromocholestanone-3	1756	1.23	38	[e,e]	α,α
Androstanol-17α-one-3	1720	2.39	..	..	.....
2-Bromoandrostanol-17α-one-3	1733	1.90	13	[e]	α
2-Bromoandrostanol-17α-one-3-hexahydrobenzoate	1739	..	19	[e]	α
Coprostanone-3	1716	..	..	..	.....
4-Bromocoprostanone-3	1733	1.87	17	[e]	β
2,4-Dibromocoprostanone-3[d]	1756	..	40	[e,e]	β,β
7-Ketones					
Pregnanone-7	1710	..	..	..	.....
6-Bromo-7-keto-3α,12α-diacetoxycholanic acid methyl ester	1737	..	27	[e]	α
11-Ketones	1713[h]	..	..	..	.....
12α-Bromo-11-keto-3α-acetoxyetiocholanic acid methyl ester[g]	*1736*, 1714	..	1	[e,p]	α
12α-Bromopregnanol-3α-dione-11,20-acetate	*1736*, 1709	..	−4	[p]	α
12α-Bromopregnanediol-3α-21-dione-11,20-diacetate[g]	*1755**, *1732**, 1716*	..	3	[p]	α
12α-Bromo-11-keto-3α-methyl succinoxycholanic acid methyl ester[g]	*1738*, 1710	..	−3	[p]	α
12-Ketones					
Pregnanone-12	1710	..	..	..	.....
11α-Bromo-12-keto-3-acetoxycholanic acid methyl ester[g]	1736	8.28	26	[e]	α
11β-Bromo-12-keto-3-acetoxycholanic acid methyl ester[g]	*1738*, 1706	8.85	−4	[p]	β
11-Bromopregnanediol-3,20-one-12-diacetate[g]	1736*	..	26	[e]	α
11-Bromo-12-keto-3α,7α-diacetoxycholanic acid methyl ester[g]	1740	..	30	[e]	α
20-Ketones					
Allopregnanone-20	1710*	..	..	..	.....
17α-Bromoallopregnanone-20[g]	1705*	..	−5	[p]	See text
Allopregnanol-3α-one-20[f]	1700*	..	..	..	
21-Bromopregnanediol-3α,17α-one-20-acetate-3[f,g]	*1730**, 1722*	..	22	..	See text
21-Bromopregnanediol-3α,17α-one-20[f,g]	1720*	..	20	..	See text
21-Bromopregnanol-17α-dione-3,20[f,g]	1716*, *1700**	..	16	..	See text

[a] Solvent CS_2 unless otherwise indicated. [b] Intensity units are moles^{-1} liter cm.$^{-2}$ × 10^4 (see ref. 4); (*) indicates measurement with sodium chloride prism (see Experimental section). Italicized figures indicate absorption maxima not associated with the α-bromo-ketone group. [c] Iodination. [d] C. Djerassi and G. Rosenkranz, *Experientia*, **7**, 93 (1951). [e] Equatorial bond. [f] Chloroform solvent. [g] Compound synthesized at the Sloan-Kettering Institute by Dr. T. F. Gallagher. The sources of other compounds have been acknowledged in previous publications. [h] Averaged value, see ref. 7. [p] Polar bond.

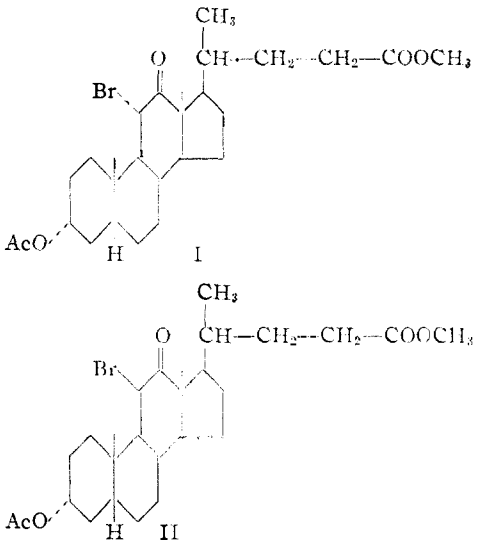
pounds, I and II are of special interest, since they provide a pair of stereoisomers in which the 11α- and 11β-configurations of the bromine atoms are well established.[5,6] The spectra of these stereoisomers are compared in Fig. 1. The 11α-bromo-12-ketone possesses one maximum at 1735 cm.$^{-1}$ while two bands, at 1706 and 1738 cm.$^{-1}$, occur in the spectrum of the 11β-bromo-12-ketone.

The band at 1706 cm.$^{-1}$ can be assigned unequivocally to the 12-ketone group in the 11β-bromo-12-ketone[3,7] and in the case of the 11α-bromo-12-ketone it is quite clear from consideration of the band intensity that the 11-ketone band has been displaced upwards and is superimposed on the absorption of the acetate and carbomethoxy groups. The integrated absorption intensities observed for the 3-acetate, the carbomethoxy, and the 12-ketone groups are 3.24, 3.13 and 2.27 units, respectively.[4] In the absence of any bromine effect, an intensity of 8.64 units would therefore be predicted for the total carbonyl absorption of these isomers. This agrees satisfactorily with the observed value of 8.85 units for the 11β-bromo-12-ketone; the slightly lower value of 8.28 units for the 11α-bromo-12-ketone is also consistent with the diminution in intensity of 0.66 unit observed to accompany a positive frequency displacement in α-brominated 3-ketones. It should be noted that the intensity

(5) E. Seebeck and T. Reichstein, *Helv. Chim. Acta*, **26**, 536 (1943).

(6) T. F. Gallagher and W. P. Long, *J. Biol. Chem.*, **162**, 495, 521 (1946).

(7) R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **71**, 241 (1949).



observed for curve A is much too high to be accounted for by the 3-acetoxy and the carbomethoxy groups alone, which would contribute only 6.37 units.

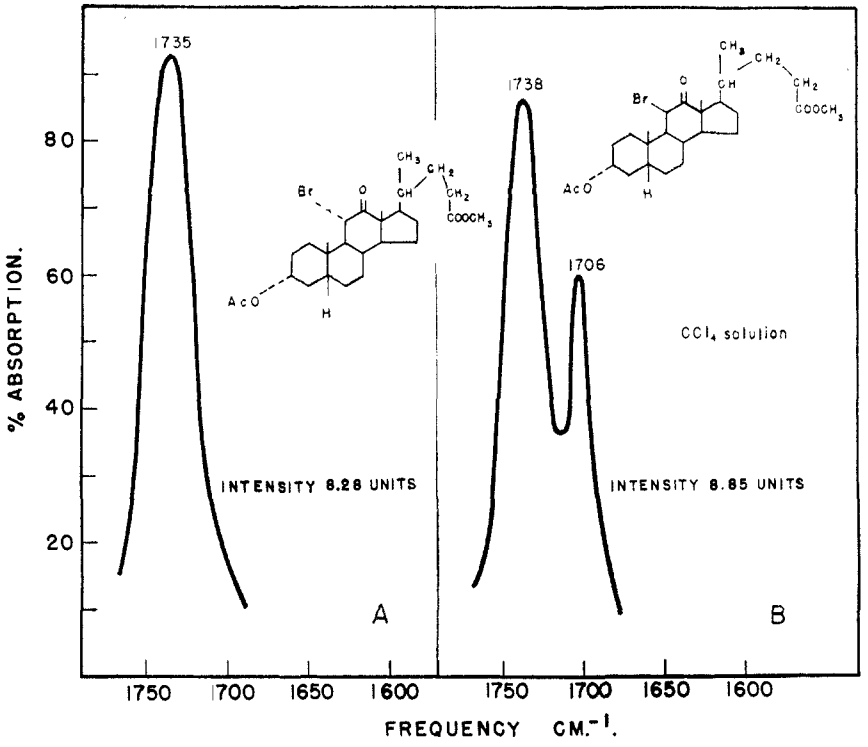


Fig. 1.—The infrared spectra of stereoisomeric 11-bromo-12-ketosteroids in the C=O stretching region.

For the four *12-bromo-11-ketones*, included in Table I the carbonyl band is not significantly displaced by bromination. In the *20-ketone series*, bromination at C-21 shifts the carbonyl frequency by about 20 cm.$^{-1}$, but bromination at the 17α-position has a negligible effect. No 17β-bromo-20-ketones have been examined.

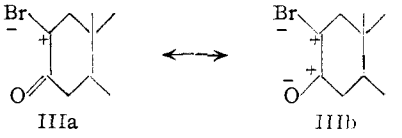
Interpretation of the Bromination Frequency Shifts.—The importance of the steric configuration of the C–Br bond in determining the effect of the bromine substituent on the carbonyl frequency is clearly established in the case of the stereoisomeric 11-bromo-12-ketones I and II. A rational explanation of this steric specificity may be suggested by consideration of the equatorial or polar conformation of the C–Br bond in the different stereoisomers,[8] and this explanation can be generalized to the other positions in the ring system.

There are three factors which might be expected to influence the vibration frequency of the carbonyl bond when a bromine atom is substituted at the α-carbon atom; (i) a mass effect, (ii) an electromeric effect transmitted from the C–Br bond through the C–C bond to the C=O bond, and, (iii) a Coulombic field effect produced by the C–Br dipole on the C=O bond.

It seems highly unlikely that an *increase* in the carbonyl frequency could be explained by a mass effect when a light hydrogen atom is replaced by a heavy bromine atom. No definite conclusion can be reached about this without carrying out a normal coördinate analysis of the vibrations, but it is also discounted by the fact that an α-iodine substituent produces a *smaller* frequency displacement than an α-bromine substituent.

It is also difficult to see how the steric relations found above can be explained adequately in terms of an electromeric effect, but a rational explanation of *all* the data so far obtained can be derived on the basis of a field effect. This will be illustrated by consideration of the bromination of the 3-ketone.

If the A ring of the steroid nucleus is regarded as cyclohexanone ring in the "chair" configuration, the carbonyl group at position 3 lies approximately in the "plane" of the ring, and the two C–H bonds at position 2 are arranged so that while one lies approximately in the plane of the ring (the equatorial bond) the other is perpendicular to this plane (the polar bond).[9] A similar disposition exists at carbon atom 4. If a bromine atom is introduced at position 2 in the equatorial position, the C–Br and C=O bonds will be approximately coplanar and the polarity of C–Br bond will reduce the polarity of the C=O bond by suppressing the contribution of structure IIIb to the resonance. This



(8) D. H. R. Barton, *Experientia*, **6**, 316 (1950).
(9) See structure XIII of reference 8.

would raise the frequency of the carbonyl vibration. If, on the other hand, the bromine atom is substituted at a polar position, the C–Br and C=O dipoles lie approximately perpendicular to one another and the field effect and accompanying change of vibration frequency would be expected to be small.

Since the substitution of a bromine atom at position 2 increases the frequency, this bromine may be presumed to substitute equatorially; the second bromine atom in the 2,2-dibromo-3-ketone has to substitute at the polar position and is observed to produce little further change in the carbonyl frequency. In the case of the 2,4-dibromo-3-ketones it is presumed that both bromine atoms substitute equatorially thus explaining the observation that the carbonyl frequency shift is approximately doubled. It is therefore suggested that *large positive shifts of the C=O stretching frequency on α-bromination in the cyclohexanone ring system in the chair configuration occur only when the bromine atom occupies an equatorial position.*

The above argument can also be extended to account for the intensity changes observed on bromination; a diminution in the intensity is evidence of a reduction in the change of dipole moment with internuclear distance during the vibration, and this might be expected to accompany a reduction in the dipole moment of the bond itself. The smaller effect of the iodine atom is also consistent with this explanation since the C–I dipole is smaller than the C–Br dipole (*cf.* CH_3–Br 1.79 debye; CH_3–I 1.60 debye).[10]

Assignment of C–Br Bond Configurations.—The stereochemical configurations of the C–Br bonds suggested on this basis are given in column vi of Table I. In the case of the 11-bromo-12-ketone stereoisomers considered above, the configurations so derived agree with those deduced from chemical considerations,[5,6] but the structures proposed above for 2- and 4-bromo-3-ketones differ from those suggested by Djerassi on the basis of molecular rotation and kinetic considerations.[11,12]

For 12-bromo-11-keto-3α-acetoxyetiocholanic acid methyl ester, the maximum at 1714 cm.$^{-1}$ must be assigned to the 11-ketone vibration. Here the shift on bromination is negligible. A 12α-bromo (polar) configuration is indicated which is in accord with the configuration assigned by Mattox, Turner, McKenzie, Engel and Kendall to the corresponding cholanic acid derivative.[13] The configuration of the other three 12-bromo-11-ketones agrees with the predictions of Gallagher, Borgstrom and Kritchevsky[14,15] based on the "rule of the rear."

The concept of polar and equatorial bond conformations cannot be applied to the brominated 20-ketones; although the 17α-bromine bond is polar with respect to the C-ring, the carbonyl group is on a side chain. The 17α-bromo-20-ketone shows no bromine shift and steric interference with the 13-methyl group may be keeping the bromine and oxygen atoms apart. In the 21-bromo-20-ketones where a positive frequency shift occurs there is presumably free rotation about the C_{20}–C_{21} bond.

Effects of α-Bromination on Ultraviolet Spectra.—The conformation of the C–Br bond appears also to influence the position and intensity of the ultraviolet absorption band of the carbonyl chromophores. In 1938 Heilbron and collaborators[16] drew attention to the fact that of two 6-bromo-7-ketosteroids stereoisomeric at position 6, one had an ultraviolet absorption spectrum closely resembling that of the non-brominated compound, but in the spectrum of the second stereoisomer the carbonyl maximum was displaced bathochromically and enhanced in intensity.

Concluding Remarks

The bromination of ketosteroids is a reaction employed extensively in steroid chemistry. The extent and position of bromination is often unpredictable on purely chemical grounds, and the positive displacement of the carbonyl stretching band has been utilized as evidence of the introduction of an α-bromine atom.[17] The magnitude of the shift has also been used to distinguish between 2,2- and 2,4-dibromo-3-ketones.

Since it has been demonstrated above that α-bromination may occur without inducing a carbonyl frequency shift, as in the 11β-bromo-12-ketones, 12α-bromo-11-ketones and 17α-bromo-20-ketones, caution must be employed in the interpretation of the infrared data. If the arguments developed above are of general application it would also be anticipated that bromination of 3-ketones of the normal series at the 2α- or 4α- (polar) positions should leave the carbonyl band position unchanged and the same would hold true for 2β- and 4β-bromo-3-ketosteroids of the allo series. It must be noted finally that these predictions are based on a chair configuration for the A ring. If, in the 2- and 4-bromo-3-ketones the A ring adopts a boat configuration, the carbonyl group can be inclined steeply to the mean plane of the ring, and the sharp distinction between the effects of polar and equatorial C—Br bonds on the C=O bond polarization may no longer be observed.

The concept of bond conformation appears to be of considerable significance and it is anticipated that other correlations between the infrared absorption spectra and the molecular structure of cyclohexane derivatives based on this concept will be forthcoming.

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(10) See G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall Inc., New York, N. Y., 1941, p. 135.

(11) C. Djerassi, THIS JOURNAL, **71**, 1003 (1949).

(12) C. Djerassi, *J. Org. Chem.*, **12**, 823 (1947).

(13) V. R. Mattox, R. B. Turner, B. F. McKenzie, L. L. Engel and E. C. Kendall, *J. Biol. Chem.*, **173**, 283 (1948).

(14) E. Borgstrom and T. F. Gallagher, *ibid.*, **177**, 951 (1949).

(15) T. F. Gallagher and T. H. Kritchevsky, THIS JOURNAL, **72**, 882 (1950).

(16) T. Barr, I. M. Heilbron, E. R. H. Jones and F. S. Spring, *J. Chem. Soc.*, 334 (1938).

(17) B. A. Koechlin, T. H. Kritchevsky and T. F. Gallagher, *J. Biol. Chem.*, **184**, 393 (1950).

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Total Synthesis of Estrone and Three Stereoisomers Including Lumiestrone

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The total synthesis of four of the eight possible racemates having the estrone structure has been described. One of these proved to be the *dl*-form of the natural hormone, and has been resolved. Another has been identified as lumiestrone. The synthetic scheme employed is summarized below. The potassium salt of *m*-methoxyphenylacetylene (prepared from *m*-hydroxyacetophenone) was added to decalin-1,5-dione in a 1:1 molecular ratio. The acetylenic bond of the resulting carbinols α and β VII (R = OCH_3) was hydrogenated to give the reduced carbinols α and β VIII (R = OCH_3). Direct cyclodehydration of either isomer with aluminum chloride afforded mainly one stereoisomeric form (α) of the tetracyclic ketone X (R = OCH_3). Dehydration of the α and/or β reduced carbinols gave the unsaturated ketone IX (R = OCH_3), which on cyclization was converted to three (α, β and γ) forms of X (R = OCH_3). Each of these was converted to the benzylidene derivatives XI (R = OCH_3, Ar = C_6H_5) the γ-isomer yielding the same product as the β. Treatment with potassium *t*-butoxide and methyl iodide gave from the α-benzylidene derivative two methylation products XII (R = OCH_3, Ar = C_6H_5) α^1 and α^2 which were epimeric at the carbon holding the angular methyl group. Similarly the β-benzylidene derivative yielded the epimeric β^1- and β^2-methylated products XII (R = OCH_3, Ar = C_6H_5). Ozonization of each of the methylation isomers gave the corresponding α^1-, α^2-, β^1- and β^2-homomarrianolic acid methyl ethers XIII (R = OCH_3), which on cyclization afforded the α^1-, α^2-, β^1- and β^2-estrone methyl ethers XIV (R = OCH_3). Demethylation yielded the α^1-, α^2-, β^1- and β^2-estrones XIV (R = OH). The β^2-isomer proved to be the racemic form of the natural product, and the β^1, that of lumiestrone, thus proving that Butenandt's postulated (C_{13} epimeric) configuration for the latter was correct. The relationship of our products to those of Anner and Miescher is discussed. A similar sequence of reactions was studied up through the formation of the tetracyclic ketones X (R = H) in the series lacking the methoxyl group. The structures of the cyclization products in both series were established by dehydrogenation experiments. A number of by-products were isolated in the course of the study, and structures for these are postulated. In an attempted estrone synthesis according to a scheme previously used successfully for the synthesis of equilenin, the cyanoketone I (R = CN) was prepared. The condensation with succinic ester failed, apparently due to opening of ring C by alcoholysis. Experiments with the analogous cyanoketone containing a double bond between rings B/C also were unpromising.

Introduction.—More than fifteen years ago extensive research programs directed toward the total synthesis of the female sex hormone estrone were already in progress.[6] In the years that followed, studies in this field continued with expanding interest in laboratories all over the world, and several tetracyclic compounds having structures similar to estrone were prepared.[7] The first unequivocal synthesis of the estrone structure was accomplished in 1942 by Bachmann, Kushner and Stevenson,[8] who isolated one of the eight possible *dl*-forms ("estrone a") from the mixture produced by attaching ring D to the keto ester I (R = $COOCH_3$, double bond between rings B/C) according to a method developed in the equilenin synthesis.[9]

In 1948 Anner and Miescher[10] prepared the saturated keto ester I (R = $COOCH_3$) of Bachmann[8] and Robinson[11] in quantity and separated three of the four possible *dl*-modifications in crystalline form. Utilizing the Bachmann method of attaching ring D, they were able to convert these keto esters into five estrones (a, b, d, e and f). The originally reported[10] sixth isomer, "estrone c," was later withdrawn,[12] since it proved to be a degradation product of isomer e. Isomer b was shown to be *dl*-estrone by resolution, and the first total synthesis of the hormone was thus realized. One of the stereoisomers appeared to be identical with that of Bachmann, Kushner and Stevenson[8] and was accordingly labeled "estrone a." Anner and Miescher[12] have also postulated that isomer f is *dl*-lumiestrone.

In the present paper we are reporting the results of our studies of a fundamentally different approach to the estrone structure. This work has culminated in a total synthesis of estrone as well as three of the (*dl*) stereoisomers, including authentic lumiestrone.[13] Some stereochemical considerations and the relationship of our products to those of Anner and Miescher are discussed.

(1) Watumull Fellow 1947–1949; Wisconsin Alumni Research Foundation Postdoctoral Fellow 1948–1949.

(2) National Institutes of Health Predoctoral Fellow 1948–1950.

(3) Wisconsin Alumni Research Foundation Postdoctoral Fellow, summer 1947.

(4) Wisconsin Alumni Research Foundation Postdoctoral Fellow, 1945–1946.

(5) Wisconsin Alumni Research Foundation Research Assistant, 1948–1951; du Pont Grant-in-Aid Research Assistant, summer 1951.

(6) See for example, R. Robinson and E. Schlittler, *J. Chem. Soc.*, 1288 (1935).

(7) *Cf.* for example the products of E. Dane and J. Schmitt, *Ann.*, **537**, 246 (1939), and of S. Breitner, *Med. u. Chem.*, **4**, 317 (1942), which probably are structural isomers of estrone. See J. Heer and K. Miescher, *Helv. Chim. Acta*, **31**, 219 (1948).

(8) W. E. Bachmann, S. Kushner and A. C. Stevenson, THIS JOURNAL, **64**, 974 (1942).

(9) W. E. Bachmann, W. Cole and A. L. Wilds, *ibid.*, **62**, 824 (1940).

(10) G. Anner and K. Miescher, *Experientia*, **4**, 25 (1948); *Helv. Chim. Acta*, **31**, 2173 (1948); *ibid.*, **32**, 1957 (1949).

(11) The ethyl ester I (R = $COOC_2H_5$) was first prepared by R. Robinson and J. Walker, *J. Chem. Soc.*, 747 (1936); 183 (1938), who also described preliminary experiments on the attachment of ring D.

(12) G. Anner and K. Miescher, *Helv. Chim. Acta*, **33**, 1379 (1950).

(13) For a preliminary report of this work see (a) W. S. Johnson, D. K. Banerjee, W. P. Schneider and C. D. Gutsche, THIS JOURNAL, **72**, 1426 (1950); (b) W. S. Johnson and L. J. Chinn, *ibid.*, **73**, 4987 (1951).