From the fact that the infrared shift is the same in the α-haloindanones as in the α-halocamphors, one would expect the angles between the carbonyl and the carbon–halogen dipoles to be the same in the two cases, and therefore the dipole moment arising from this part of the molecule to be the same. However, that does not mean the over-all dipole moment will be the same because the phenyl ring in the α-haloindanones would be expected to give rise to a dipole of about 0.4 D. in approximately the opposite direction to that of the resultant of the C=O and C—X dipole, and, therefore, one would expect the α-haloindanones to have lower moments by about this amount. With the exception of the moment of 1-chloro-2-indanone in dioxane, this is the case. The four cases of the two α-haloindanones, measured in heptane and benzene, have lower moments than the corresponding α-halocamphors by from 0.14 to 0.63 D. with an average of 0.37 D.

That the moment of the α-haloindanones differed in the solvents by 0.19, 0.33 and 0.38 D., while the moment of the α-halocamphors differed by only 0.01, 0.01, 0.30, 0.04, 0.00 and 0.11 D. suggests that the α-haloindanone system is not as rigid as the α-halocamphor system. In a previous paper,[10] it was observed that the n.m.r. peak for the two hydrogens on the number 3 carbon in the case of 1-bromo-2-indanone was much broader than in the case of the corresponding chloro compound, which suggests a change in the ring with the heavier bromine attached, indicating some flexibility.

The fact that 1-bromo-2-indanone has a smaller moment than the corresponding chloro compound while in the camphor series the chloro and bromo compounds have the same moment may result from a larger induction in the more polarizable bromine by phenyl.

The moment of 2-bromo-4-phenyl-cyclohexanone is considerably lower than that of the other compounds and is the same in heptane and dioxane. The fact that the moment does not vary with solvent indicates this is not a mixture of axial and equatorial forms, and the fact that the moment is as small as it is suggests the bromine is in the axial position. The dipole moment of this compound with bromine axial can be calculated from the moment of trans-2-bromo-4-t-butylcyclohexanone of 3.20 D.[2] which is known to have the bromine axial. The phenyl group gives rise to a moment of 0.40 D., which makes an angle of about 140° with the resultant of the C=O and C—Br dipoles. This reduces the resultant by 0.30 D. so the calculated moment of 2-bromo-4-phenyl-cyclohexanone would be 3.20 D. − 0.30 D. = 2.90 D., a value in excellent agreement with the observed moment.

The Synthesis of cis-9-Carbomethoxy-1a-carbomethoxymethyl-8-methyl-cis-1,1a,2,3,4,-4a-Hexahydrofluorene, A Degradation Product of Gibberellic Acid[1]

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The racemate of the title compound has been synthesized and shown to be identical, but for lack of optical activity, with a transformation product of epiallogibberic acid 3, a degradation product of gibberellic acid 1.

The reaction of gibberellic acid (1) with boiling hydrazine hydrate has been found[2] to yield allogibberic acid (2, m.p. 196–198°) and epiallogibberic acid (3, m.p. 244°) via the intermediate gibberellenic acid 4. Subsequent transformations[2,3] furnished the keto diesters 5 (m.p. 205–207°) and 6 (m.p. 168–169°) and demonstrated[2] the epimeric relationship at position 4a between the hexahydrofluorenes 5 and 6. Both these studies[2] and other work[4] has supported the stereochemistry indicated in structures 2, 3, 5 and 6.

We have reduced each of the keto esters 5 and 6[5] to the corresponding diesters 7 (m.p. 118.5–119.5°) and 8a (m.p. 101° or 124°) by the reaction of the ketones with 1,2-ethanedithiol and then desulfurization with Raney nickel.

As confirmation of the aforementioned structural and stereochemical assignments we have synthe-

sized the racemate of structure 8. Our synthesis utilized the previously described[6] hydroxy ester 9 which was converted by reaction with hydrogen bromide in ether to a mixture of the crude bromo ester 10 and the crystalline lactone 11. As noted previously,[6] saponification of the lactone 11 followed by acidification of the corresponding salt of the hydroxy acid resulted in immediate formation of the starting lactone.

Reaction of the crude bromide 10 with sodium cyanide in dimethyl sulfoxide afforded a mixture of cyano esters isolated as the cyano acids 12 and 13. Each of these cyano acids 12 and 13 was converted to the corresponding amide acids 14a and 14b which were converted to the esters 15a and 15b by reaction with diazomethane. Heating the amide acid 14 or reaction of the ester 15b with sodium methoxide afforded the imide 16. Hydrolysis of this imide 16 followed by esterification of the resulting acid mixture with diazomethane yielded the ester 15a and a new ester 17. Inspection of molecular models leaves no doubt that the

(1) This research has been supported by National Science Foundation Grant, No. G9486.

(2) J. F. Grove and T. P. C. Mulholland, J. Chem. Soc., 3007 (1960).

(3) T. P. C. Mulholland, ibid., 2693 (1958).

(4) G. Stork and H. Newman, J. Am. Chem. Soc., 81, 3168 (1959).

(5) We are indebted to Dr. J. F. Grove for supplying us with a sample of this substance.

(6) H. O. House, V. Paragamian and D. J. Wluka, ibid., 82, 2561 (1960).

1. HSCH₂CH₂SH │ 2. RaNi   1. HSCH₂CH₂SH │ 2. RaNi

8a, R = Me
b, R = H
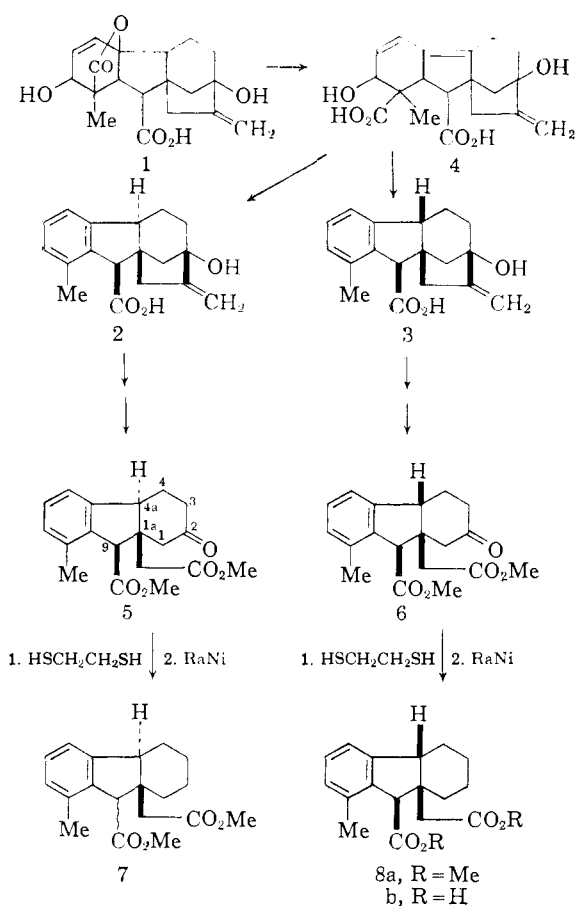
isomer **16** having the six-membered imide ring and the five-membered carbocyclic ring fused *cis* will be more stable than the diastereoisomer in which the ring fusion is *trans*. Therefore the indicated stereochemistry could be assigned to compounds **12** to **17**.

Treatment of either cyano acid **12** or **13**, or the imide **16** with refluxing 48% hydrobromic acid, afforded the diacid **18**, and a small amount of the imide **16** in each case. When the reaction was stopped after partial hydrolysis, the imide **16** was the major product, suggesting that this compound is the intermediate in the acid hydrolysis. The diacid **18** was converted to the corresponding anhydride **19** which may be assigned the indicated *cis* stereochemistry for the same reasons given above for the imide **16**. Hydrolysis of the anhydride **19** with water regenerated the diacid **18**, showing that the two acid functions are disposed *cis* to each other. When the anhydride was treated with anhydrous ammonia in ether and the resulting amide acid was methylated with diazomethane, the amide ester **17** was obtained. Hence no changes in the ring skeleton had occurred during the vigorous acid hydrolysis of the cyano acids **12** and **13** or the imide **16**. The diacid **18** can therefore be assigned the indicated stereochemistry. Methylation of the diacid **18** with diazomethane afforded a diester **20** isolated in two crystalline forms melting at 99.5 to 100.5° and at 123 to 124°. The diester **20** could be saponified to regenerate the diacid **18**. The failure to observe partial

epimerization during the saponification may be attributable to the intervention of the anhydride **19** as an intermediate in the saponification. The comparable intervention of anhydride intermediates has been observed[7] in the saponification of the monoesters of succinic and glutaric acids.

The diacid samples **8b** (from degradation) and **18** (from synthesis) have identical infrared and ultraviolet spectra and do not depress one another's melting point. Similarly, the diester **8a** (from degradation, m.p. 102–103°) and **20** (racemate from synthesis, m.p. 99.5–100.5°) have identical infrared and ultraviolet spectra and a mixture of the two samples melts at 99.5–102.5°. The diester, m.p. 121–125°, previously obtained[2,5] as a by-product in the degradation of epiallogibberic acid also has infrared and ultraviolet spectra identical with the spectra of the optically active diester **8a** and the racemic diester **20** and is apparently the second crystalline form of the optically active diester **8a**.

Experimental[8]

cis- and *trans*-1a-Carboxymethyl-9-cyano-8-methyl-1,1a,-2,3,4,4a-*cis*-hexahydrofluorene (**12** and **13**) and 1a-Carboxymethyl- 9- hydroxy- 8- methyl - 1,1a,1,2,3,4,4a- *cis* - hexahydrofluorene Lactone-(11).—A solution of the hydroxy ester **9** (10 g. or 0.036 molé) in 150 ml. of anhydrous ether was cooled to 5° and saturated with dry hydrogen bromide. The resulting mixture was stirred at 5° for 1.5 hr. and then poured onto ice. The organic layer was separated, washed successively with aqueous sodium bicarbonate and water and dried over magnesium sulfate. Removal of the solvent left 12.4 g. of a light yellow oil with infrared absorption[9] at 1735 cm.⁻¹ (C=O of an ester) and a shoulder at 1780 cm.⁻¹ (C=O of a α-lactone). A solution of this oil in 50 n.l. of freshly distilled dimethylsulfoxide was added over a period of 30 min. to a stirred solution of 5 g. (0.102 mole) of sodium cyanide in 70 ml. of dimethyl sulfoxide kept at 52°. The mixture was stirred at 52° for an additional 45 min., allowed to come to room temperature and then poured into water. The aqueous solution was extracted with ether and the ether extracts were washed with water, dried over magnesium sulfate and concentrated to leave 9.3 g. of a yellow oil. This oil was then saponified by reaction for 3 hr. with a solution of 7 g. of potassium hydroxide in refluxing methanol. The resulting solution was concentrated, diluted with water and extracted with ether. The ether extracts contained 1.7 g. of a yellow oil which was not further investigated. The aqueous layer was acidified with hydrochloric acid and extracted with ether. After the ether solution had been concentrated and the residue heated on a steam-bath for 15 min., a solution of the residue in ether was extracted with aqueous sodium bicarbonate. The organic layer was dried over magnesium sulfate and concentrated. Crystallization of the residue from aqueous methanol afforded 1.4 g. (15.8% based on the hydroxy ester **9**) of the lactone **11** as white needles, m.p. 111–112°. The lactone has infrared absorption[9] at 1780 cm.⁻¹ (C=O of a α-lactone) with a series of low intensity ultraviolet maxima[10] in the region 260–280 mμ (ε 390–440).

*Anal.* Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.45; H, 7.75.

The bicarbonate extract was acidified and extracted with ether. After the ethereal extract had been dried over mag-

(7) E. Gaetjens and H. Morawetz, *J. Am. Chem. Soc.*, **82**, 5328 (1960).

(8) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Baird, model B, or a Perkin–Elmer, model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, model 11 MS. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

(9) Determined as a solution in carbon tetrachloride.

(10) Determined as a solution in 95% ethanol.
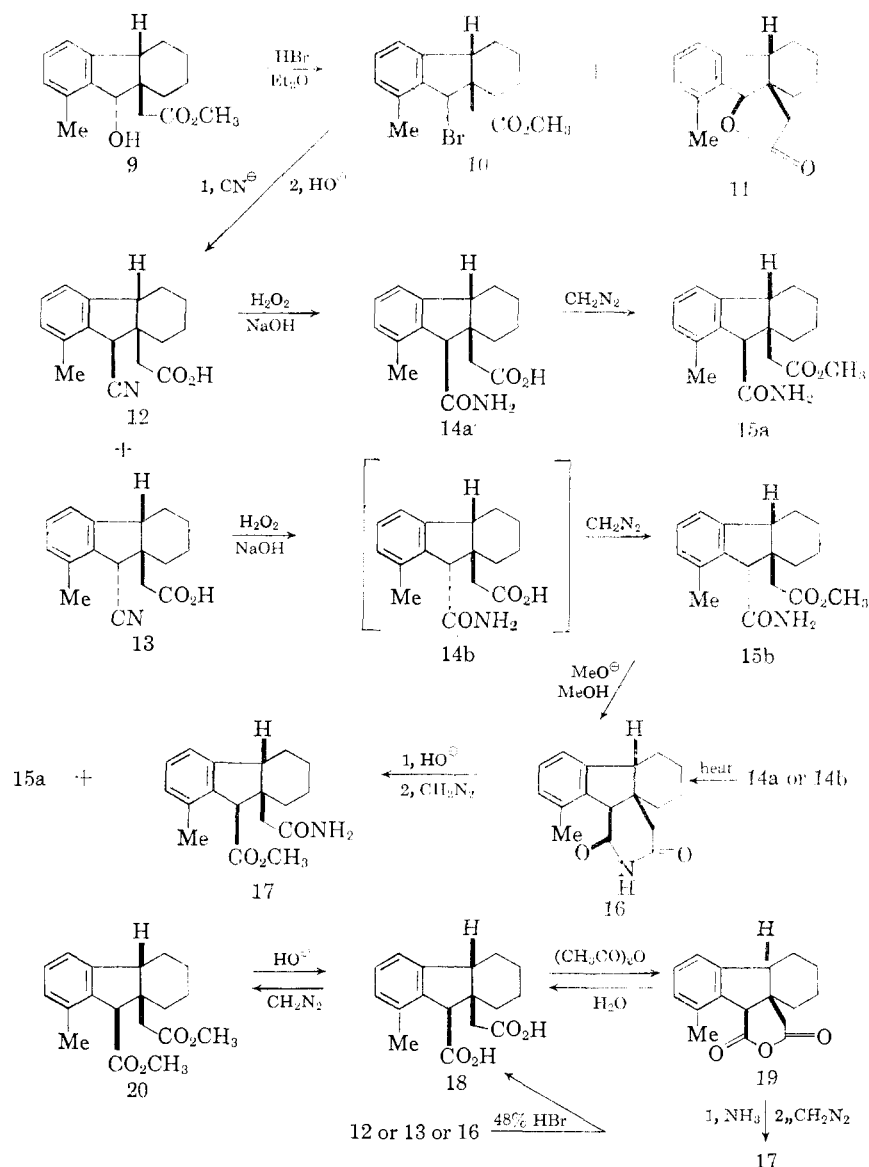
nesium sulfate and concentrated, the residue (5.5 g. or 56% based on the hydroxy ester 9) was fractionally crystallized from a hexane–ethyl acetate mixture. The fractions separated were 2.33 g. (24%) of small white prisms, m.p. 190–193°, and 0.86 g. (8.8%) of white prisms, m.p. 142–144°. A portion of the higher melting solid was recrystallized twice from a mixture of hexane and ethyl acetate to give the pure cyano acid 12 as white prisms, m.p. 194–195° with infrared absorption[11] at 2200 cm.$^{-1}$ (weak, C≡N) and at 1700 cm.$^-$ (carboxyl C=O) with a series of ultraviolet maxima[10] in the region 260–280 mμ (ϵ 200–258)

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.81; H, 6.83; B, 5.20.

A portion of the lower melting acid was recrystallized four times from an hexane–ethyl acetate mixture to separate the cyano acid 13 as white prisms, m.p. 144–145°, with infrared absorption[11] at 2240 cm.$^{-1}$ (weak, C≡N) and 1706 cm.$^{-1}$ (carboxyl C=O) and a series of ultraviolet maxima[10] in the region 260–280 mμ (ϵ 226–300). Solution infrared spectra of the two isomeric cyano acids are different indicating that the two samples are not merely different crystalline forms.

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.58; H, 6.90; N, 5.26.

(11) Determined as a suspension in a potassium bromide pellet.

In an attempt to achieve the same transformation in methanol solution, a solution of 3.0 g. (0.011 mole) of the hydroxy ester 9 in anhydrous methanol was saturated with dry hydrogen bromide. After appropriate manipulations to separate a small amount of the crude lactone 11, m.p. 111–112°, the residual neutral fraction was allowed to react with 0.75 g. (0.013 mole) of sodium cyanide in methanol for 20 hr. and then diluted with water and extracted with ether. The resulting organic product (2.46 g. of yellow oil) was saponified by reaction with 0.73 g. (0.011 mole) of potassium hydroxide in a boiling aqueous methanol for 2.5 hr. The resulting acidic product (1.35 g. or 45% based on the hydroxy ester) was crystallized from a hexane–ethyl acetate mixture to give one isomer of 1a-carboxymethyl-9-methoxy-8-methyl-1,1a,2,3,4,4a-cis-hexahydrofluorene as white prisms, m.p. 151–152°. The material exhibits infrared absorption[11] at 1705 cm.$^{-1}$ (carboxyl C=O) with a series of ultraviolet maxima[10] in the region 260–280 mμ (ϵ 254–304).

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08; CH_3O, 11.31. Found: C, 74.54; H, 7.98; CH_3O, 11.04.

1a-Carboxymethyl-9-carboxamido-8-methyl-1a,1,2,3,4,4a-cis-hexahydrofluorene (14a).—The pure cyano acid 12, m.p. 194–195° (933 mg. or 3.47 mmoles), was dissolved in 35 ml. of water containing 0.28 g. (7 mmoles) of sodium hydroxide. Hydrogen peroxide (3.0 ml. of 30% aqueous)

was added to the solution and the mixture was stirred, at room temperature, for 24 hr. An additional 1.5 ml. of hydrogen peroxide was then added and the mixture was further stirred for an additional 18 hr. and then acidified with hydrochloric acid. The resulting white solid was filtered and recrystallized from aqueous ethanol to separate 546 mg. (55%) of the acid amide 14a as short white needles, m.p 222–226° dec. A portion of this material was recrystallized twice from a mixture of hexane and ethyl acetate to give white prisms, m.p. 232–233° dec., with infrared absorption[11] at 3400 (—NH), 1695 (carboxyl C=O) and 1650 cm.$^{-1}$ (C=O of an amide) and a series of ultraviolet maxima[10] in the region 260–280 mμ (ϵ 212–292).

Anal. Calcd. for $C_{17}H_{21}NO_3$: C, 71.05; H, 7.37; N, 4.87. Found: C, 70.87; H, 7.24; N, 4.81.

Reaction of a 189-mg. sample of the amide acid 14a with excess diazomethane in a methanol–ether mixture followed by removal of the solvents and recrystallization of the residue from a hexane–ethyl acetate mixture afforded 184 mg. (93%) of the amide ester 15a, m.p. 156–157°. The product has infrared absorption[12] at 3500, 3400 and 3200 cm.$^{-1}$ (N—H), at 1723 cm.$^{-1}$ (ester C=O) and at 1675 cm.$^{-1}$ (amide C=O) with a series of ultraviolet maxima[10] in the region 260–280 mμ (ϵ 200–282).

Anal. Calcd. for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.75; H, 7.78; N, 4.76.

1a-Carbomethoxymethyl-9-carboxamido-8-methyl-1,1a,-2,3,4,4a-*cis*-hexahydrofluorene (15b).—A solution of 310 mg. (1.15 mmoles) of the cyano acid 13, m.p. 144–145°, and 70 mg. of sodium hydroxide in 30 ml. of water was treated with 4 ml. of 30% hydrogen peroxide as previously described. Crystallization of the resulting crude amide acid from a hexane–ethyl acetate mixture gave 120 mg. (37%) of a mixture of amide acids 14, m.p. 205–230° dec., which was treated with excess diazomethane. Fractional crystallization of the resulting amide esters 15 from a hexane–ethyl acetate mixture separated 43 mg. of the amide ester 15a, m.p. 156–157°, and 73 mg. of the amide ester 15b as a white solid, m.p. 133–134°. An additional crystallization raised the melting point of the amide ester 15b to 134–135°. The infrared spectrum[12] of this material has absorption at 3520, 3410 and 3200 cm.$^{-1}$ (N—H), at 1725 cm.$^{-1}$ (ester C=O) and 1680 cm.$^{-1}$ (amide C=O) and differs from the spectrum of the amide ester 15a. A series of ultraviolet maxima[10] are present in the region 260–280 mμ (ϵ 210–295).

Anal. Calcd. for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.61; H, 7.51; N, 4.67.

The Imide 16 of 9-Carboxy-1a-carboxymethyl-8-methyl-1,1a,2,3,4,4a-*cis*-hexahydrofluorene. A.—A 510-mg. (1.8 mmoles) sample of a mixture of the amide acids 14, m.p. 215–219°, was heated at 235° for 10 min. at which time the evolution of gases stopped. Trituration of the residue (481 mg.) with ether left 315 mg. of a tan solid, which was dissolved in ether and washed with aqueous sodium bicarbonate. Drying of the ether solution over magnesium sulfate and removal of the solvent left 290 mg. (61%) of a white solid, m.p. 190–193°. A portion of this solid was recrystallized from aqueous methanol to give the imide 16 as white needles, m.p. 194–195°, with infrared absorption[11] at 1680 cm.$^{-1}$ and a shoulder at 1705 cm.$^{-1}$ (imide C=O) and a series of ultraviolet maxima[10] in the region 260–280 mμ (ϵ 580–610).

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.87; H, 7.11; N, 5.38.

B.—The amide ester 15b, m.p. 134° (301 mg. or 1 mmole) was dissolved in 20 ml. of methanol and 10 ml. of a solution of sodium methoxide, prepared from 0.23 g. (0.01 g.-atom) of sodium and 25 ml. of methanol, was added. The mixture was refluxed overnight under a nitrogen atmosphere and then cooled, neutralized with acetic acid, diluted with water and extracted with ether. The ethereal extract was washed successively with aqueous sodium bicarbonate and water and then dried over magnesium sulfate. Removal of the solvent and fractional crystallization of the residue from an hexane–ethyl acetate mixture, afforded 100 mg. of one crystalline form of the imide 16 as white needles, m.p. 193–194°, and 127 mg. of a second crystalline form of the imide 16 as white needles, m.p. 180–181°.

(12) Determined as a solution in chloroform.

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 76.73; H, 7.31; N, 4.91.

The infrared spectra[11] of the two samples are identical with each other and with the infrared spectrum of the imide, m.p. 194°, previously described. When a hot solution of 60 mg. of the imide sample, m.p. 180–181°, in a mixture of hexane and ethyl acetate was seeded with the imide sample, m.p. 193–194°, and allowed to cool, 45 mg. of the imide 193–194°, separated as white needles.

A 110-mg. (0.41 mmole) sample of the imide 16 was added to 15 ml. of 5% aqueous potassium hydroxide solution and the mixture was stirred for 45 min. at room temperature, at which time all the solid had dissolved. The mixture was neutralized with hydrochloric acid and extracted with ether. The ether extract was washed with aqueous sodium bicarbonate, dried over magnesium sulfate and concentrated. Crystallization of the residue from aqueous ethanol afforded 10 mg. of the unchanged imide, m.p. 193–194°. The bicarbonate layer was acidified with hydrochloric acid and extracted with ether. After the ethereal extract had been dried over magnesium sulfate and concentrated, the residual solid (100 mg.) was subjected to fractional crystallization from a hexane–ethyl acetate mixture to separate 20 mg. of a white solid, m.p. 216–218° dec., and 50 mg. of white plates, m.p. 188–189° dec. Similar results were obtained in subsequent experiments.

A 38-mg. sample of the higher melting acidic fraction, m.p. 216–218° dec., was methylated with diazomethane as previously described. Recrystallization of the crude product (34 mg.) from a mixture of hexane and ethyl acetate afforded 28 mg. of the amide ester 15a as transparent prisms, m.p. 156–157°, identified by a mixed melting-point determination and by comparison of infrared spectra. The similar methylation of a 57-mg. sample of the lower melting acidic fraction, m.p. 188–189° dec., yielded, after crystallization from a hexane–ethyl acetate mixture, 36 mg. of the amide ester 17 as transparent prisms, m.p. 177–178°. The infrared spectrum[12] of the product has bands at 3530, 3440 and 3390 cm.$^{-1}$ (N—H), at 1725 and 1713 cm.$^{-1}$ (ester C=O and 1675 cm.$^{-1}$ (amide C=O) and differs from the spectra of the amide esters 15a and 15b. The ultraviolet spectrum[10] exhibits a series of maxima in the region 260–280 mμ (ϵ 190–276).

Anal. Calcd. for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.82; H, 7.79; N, 4.61.

1a-Carboxymethyl-9-carboxy-8-methyl-1,1a,2,3,4,4a-*cis*-hexahydrofluorene (18). A.—A mixture of 1.05 g. (3.9 mmoles) of the imide 16 and 90 ml. of freshly distilled 48% hydrobromic acid was refluxed, with stirring under a nitrogen atmosphere, for 20 hr. After the mixture had been cooled, the solid which separated was dissolved in aqueous sodium bicarbonate and the solution was washed with ether. Acidification of the bicarbonate solution followed by extraction with ether separated a white solid which was recrystallized from ethyl acetate. The diacid 18 separated as white prisms, m.p. 252–253° dec., yield 0.87 g. (83%), which exhibit infrared absorption[11] at 3000 (broad, assoc. O—H) and at 1710 cm.$^{-1}$ (carboxyl C=O) with a series of ultraviolet maxima[10] in the region 260–280 mμ (ϵ 180–254).

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.67; H, 6.91.

B.—Reaction of 0.85 g. (3.16 mmoles) of the cyano acid 13, m.p. 144–145°, with 80 ml. of boiling 48% hydrobromic acid for 18 hr. afforded 0.26 g. (28%) of the diacid 18, m.p. 252–253° dec., and 0.37 g. (44%) of the crude imide 16, m.p. 187–190°.

The Anhydride 19 of 1a-Carboxymethyl-9-carboxy-8-methyl-1,1a,2,3,4,4a-cis-hexahydrofluorene.—The diacid 18 (315 mg. or 1.1 mmoles) was added to 10 ml. of freshly distilled acetic anhydride and the mixture was refluxed for 3 hr. It was then cooled, diluted with 1.7 ml. of water and stirred at room temperature until the mixture became homogeneous. After the resulting mixture had been further diluted with water and extracted with ether, the extract was washed successively with aqueous sodium bicarbonate and water and then dried over magnesium sulfate. Removal of the solvent left 275 mg. (93%) of the crude anhydride as a white solid, m.p. 174–178°. Recrystallization from cyclohexane afforded the pure anhydride as white plates, m.p. 179.5–180.5°, with infrared absorption[12] at 1810 and 1760 cm.$^{-1}$ (anhydride C=O) and a series of ultraviolet maxima[12] in the region 260–289 mμ (ϵ 346–495).

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.30; H, 6.76.

A solution of 195 mg. (0.72 mmole) of the anhydride **19** in 50 ml. of anhydrous ether was saturated with dry ammonia. Water was then added to the mixture and the layers were separated. After the ethereal solution had been dried over magnesium sulfate and concentrated, 11 mg. of the crude, unchanged anhydride **19**, m.p. 175–180°, was recovered. The aqueous layer was acidified with hydrochloric acid and extracted with ether. The ether solution was dried over magnesium sulfate and the solvent was removed, leaving 171 mg. (83%) of crude amide acid. Recrystallization from a hexane–ethyl acetate mixture afforded 154 mg. (75%) of the pure amide acid as white prisms, m.p. 187–189° dec.

A 74-mg. sample of this amide acid was methylated with diazomethane as previously described. The product, recrystallized from a hexane–ethyl acetate mixture, consisted of 71 mg. (92%) of the amide ester **17** as white prisms, m.p. 177–178°, identified by a mixed melting-point determination and comparison of infrared spectra.

A mixture of 46 mg. (0.17 mmole) of the anhydride **19** and 10 ml. of water was refluxed for 1.5 hr., with stirring, and then cooled and extracted with ether. The ether extract was washed with aqueous sodium bicarbonate, dried over magnesium sulfate and concentrated. Crystallization of the residue from cyclohexane afforded 19 mg. (41%) of the unchanged anhydride, 179–180°. The bicarbonate extract was acidified with hydrochloric acid and extracted with ether. After the ether solution had been dried over magnesium sulfate and concentrated, recrystallization of the residue from ethyl acetate afforded 29 mg. (59%) of the diacid **18** as white prisms, m.p. 251.5–253.5° dec. A mixed melting point with the diacid obtained by the hydrolysis of the imide was not depressed and the infrared spectra of the two samples are identical.

9-Carbomethoxy-1a-Carbomethoxymethyl-8-methyl-*cis*-1,1a,2,3,4,4a-hexahydrofluorene (20).—The diacid **18** (1.23 g. or 4.3 mmoles), obtained by hydrolysis of the cyano acid, was methylated with diazomethane as described previously. The crude product was recrystallized from aqueous methanol to separate 1.16 g. (87%) of the pure diester **20** as white needles, m.p. 99.5–100.5°, with infrared absorption[9] at 1737 cm.$^{-1}$ (ester C=O) and a series of ultraviolet maxima[10] in the region 260–280 mμ (ε 170–260).

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 71.97; H, 7.77.

When the diester was recrystallized several times from hexane, it separated as a second crystalline form, melting at 123–124°. The infrared spectra[10] of the two samples are identical. When a sample of the crystalline form, m.p 123–124°, was recrystallized once from aqueous methanol, it separated as white needles, m.p. 99.5–100.5°.

The similar methylation of 81 mg. (0.27 mmole) of the diacid **18**, obtained by the hydrolysis of the anhydride **19**, afforded, after recrystallization from aqueous methanol, 65 mg. (81%) of the diester **20** as white needles, m.p. 99.5–100.5°. The melting point of a mixture of this sample with the diester described above was not depressed and the infrared spectra[9] of the two samples are identical.

A solution of 200 mg. (0.63 mmole) of the diester **20** and 0.8 g. of sodium hydroxide in 20 ml. of aqueous methanol was refluxed for 4 hr. and then cooled, concentrated under reduced pressure, diluted with water and extracted with ether. After the aqueous layer had been acidified with hydrochloric acid and extracted with ether, the ether extract was dried over magnesium sulfate and concentrated. Reaction of the crude residue (199 mg.) with diazomethane followed by crystallization of the crude product from aqueous methanol afforded 161 mg. (81%) of the diester **20** as white needles, m.p. 99.5–100.5°, identified by a mixed melting-point determination and comparison of infrared spectra.

(+)-9-Carbomethoxy-1a-carbomethoxymethyl-8-methyl-*cis*-1,1a,2,3,4,4a-hexahydrofluorene (8a).—To a solution of 200 mg. (0.6 mmole) of the keto diester **6**, m.p. 168–169°, in 1.5 ml. of chloroform was added 0.2 ml. of 1,2-ethanedithiol and 0.2 ml. of freshly distilled boron trifluoride etherate. After the mixture had been allowed to stand overnight at room temperature, it was diluted with 25 ml. of chloroform, washed successively with water and aqueous sodium chloride and then filtered through a column of 10 g. of alumina deactivated with 3 ml. of water. The column was washed with 100 ml. of chloroform and the combined chloroform solutions were concentrated under reduced pressure. The residue, a slightly yellow oil, was dissolved in 80 ml. of 70% aqueous ethanol. Raney nickel catalyst (5 g.) was added to the solution and the mixture was refluxed for 5 hr. After the mixture had been cooled and filtered, the filtrate was concentrated and a solution of the residue in ether was washed with water, dried over magnesium sulfate and concentrated. The residue was saponified by reaction with 0.6 g. of sodium hydroxide in aqueous methanol for 3 hr. The mixture was cooled, concentrated, diluted with water and extracted with ether. After the aqueous layer had been acidified with hydrochloric acid and extracted with ether, the extract was dried over magnesium sulfate and concentrated to leave 81 mg. (47%) of the crude diacid as a yellow oil. A solution of this oil in a hexane–ethyl acetate mixture deposited 60 mg. of colorless prisms, m.p. 248–252°. A further recrystallization from ethyl acetate gave 56 mg. of the pure diacid **8b** as colorless prisms, m.p. 251–253° dec. The infrared[11] and ultraviolet[10] spectra of this material are identical with the spectra of the synthetic diacid **18** and the melting point of a mixture of the two samples was not depressed.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.53; H, 7.03.

A 40-mg. sample of this diacid **8b** was methylated with diazomethane in the usual manner to yield 42 mg. of a neutral white solid. Two recrystallizations from aqueous methanol gave 35 mg. of the pure diester **8a** as white needles, m.p. 102–103°, [α]D + 32° (c 1.00 in chloroform). The infrared[9] and ultraviolet[10] spectra of this material are identical with the spectra of the synthetic diester **20**. A mixture of the optically active diester **8a**, m.p. 102–103°, and the racemic diester **20**, m.p. 99.5–100.5°, melted at 99.5–102.5°.

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 72.41; H, 7.90.

The infrared[9] and ultraviolet[10] spectra of the previously reported[2] diester, prisms from ether–petroleum ether melting at 121–125°[5], are also identical with spectra of the diesters **8a** and **20**. We therefore conclude that this diester sample, m.p. 121–125°, is the second crystalline form of the optically active diester **8a**, m.p. 102–103°, described here.

(−)-9-Carbomethoxy-1a-carbomethoxymethyl-8-methyl-1,1a,2,3,4,4a-trans-hexahydrofluorene (7).—Degradation of gibberellic acid as described[3] afforded a sample of the keto diester **5** as white crystals, m.p. 206.5–209°, [α]D +9° (c 1.04 in chloroform), [lit.[2,3] m.p. 205–207°, [α]^{24}D + 17° (c 0.20 in acetone)]. To a solution of 210 mg. (0.64 mmole) of this keto diester in 1 ml. of chloroform was added 0.2 ml. of boron trifluoride etherate and 0.2 ml. (250 mg. or 2.66 mmoles) of 1,2-ethanedithiol. The procedure previously described was followed. The residual diester **7**, from the Raney nickel treatment, crystallized from aqueous methanol as white needles, m.p. 118.5–119.5°, yield 95 mg. (47%), [α]D −24° (c 1.03 in chloroform). The sample exhibits infrared absorption[9] at 1735 cm.$^{-1}$ (ester C=O) with a series of ultraviolet maxima[19] in the region 260–280 mμ (ε 285–370). The infrared spectrum of the diester **7** is definitely not identical with the spectra of the diesters **8a** and **20**.

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 71.93; H, 7.63.