

Acidic Aromatic Hydrocarbons. Analogs of Fluoradene

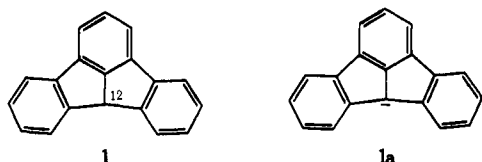
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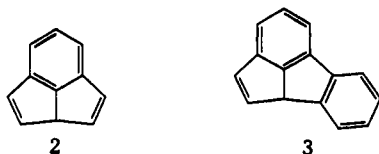
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As part of a study of the debenzo analogs of fluoradene (1), which were predicted to be more acidic than the parent compound ($pK_a \cong 11$), 1*H*-cyclopent[*cd*]indene (11) was prepared. It could not be isomerized to 2*aH*-cyclopent[*cd*]indene (2) through protonation of the anion, and had a $pK_a \geq 18-20$. 9*bH*-Cyclopenta[*jk*]fluorene (3) also was synthesized, but the absence of proton exchange in tritiated ethanol and the lack of anion formation in methanolic sodium methoxide indicated that, contrary to expectation, it was less acidic than fluoradene.

Fluoradene (1) was prepared as one of a series of aromatic hydrocarbons containing a benzene ring warped out of planarity by fused cyclopentano ring systems,² and it had the properties expected for such a strained compound with decreased aromatic stabilization.^{3a} It also proved to be very strongly acidic, having a pK_a of about 11.^{3a,b} This unusual acidity can be accounted for by the high resonance stabilization of the anion 1a as compared to that of the parent hydro-



carbon 1 and relief of strain in changing the hybridization at C-12 from tetrahedral to trigonal. The "4*n* + 2" or Huckel rule⁴ for determining aromaticity obviously does not apply in the case of fluoradene anion, which has 20- π electrons. Molecular orbital calculations on 2*aH*-cyclopent[*cd*]indene (2)⁵ indicate that the order of resonance stabilization should be anion > radical > cation. This prediction holds true for fluoradene, which is the dibenzo derivative of 2, since



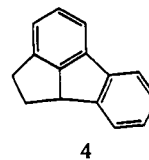
neither the radical nor the carbonium ion could be prepared.^{3a}

It was postulated^{3a} that acidity should increase in the order 1 < 3 < 2, since there would be a greater difference in resonance stabilization between the hydrocarbon and anion as the resonance contributions of the fused benzene rings are removed (*cf.* fluorene,⁶ indene,⁷ and cyclopentadiene,⁸ estimated pK_a 's 25, 21, and 17, respectively). The same order would be postulated if relief of strain were considered a major factor in the acidity.

- (1) National Institutes of Health Predoctoral Fellow.
 (2) (a) H. Rapoport and J. Z. Pasky, *J. Amer. Chem. Soc.*, **78**, 3788 (1956); (b) H. Rapoport and G. Smolinsky, *ibid.*, **82**, 1171 (1960); (c) B. L. McDowell, G. Smolinsky, and H. Rapoport, *ibid.*, **84**, 3531 (1962).
 (3) (a) H. Rapoport and G. Smolinsky, *ibid.*, **82**, 934 (1960); (b) R. Kuhn and D. Rewicki, *Justus Liebigs Ann. Chem.*, **706**, 250 (1967).
 (4) E. Huckel, *Z. Electrochem.*, **43**, 752 (1937).
 (5) R. J. Windgassen, Jr., W. W. Saunders, Jr., and V. Boekheide, *J. Amer. Chem. Soc.*, **81**, 1459 (1959).
 (6) J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932).
 (7) W. K. McEwan, *ibid.*, **58**, 1124 (1936).
 (8) D. Peters, *J. Chem. Soc.*, 1274 (1960).

It has been proposed⁹ that the acidity of a hydrocarbon can be correlated with ΔM , which is related to the difference in π -bond energy between the hydrocarbon, AH, and the corresponding anion, A⁻. Comparisons by this calculation give the following values for ΔM : fluorene, 1.523; indene, 1.747; fluoradene (1), 2.115; 9*bH*-cyclopenta[*jk*]fluorene (3), 2.276; 2*aH*-cyclopent[*cd*]indene (2), 2.411. It should be noted that these calculations assume that strain energy is the same in the hydrocarbon and the anion; however, in the case of 1, 2, and 3, less strain is anticipated in the anion.

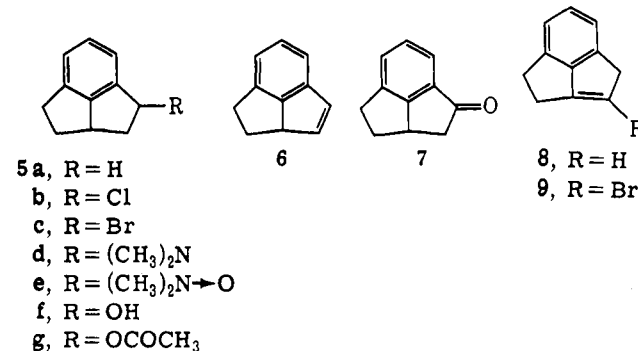
These speculations and the availability of 2,2*a*,3,4-tetrahydro-1*H*-cyclopent[*cd*]idene (5a)^{2a} and 2,9*b*-dihydro-1*H*-cyclopenta[*jk*]fluorene (4)^{2c} prompted an



investigation of the synthesis and properties of 2 and 3.

2*aH*-Cyclopent[*cd*]indene (2).—The most direct route to 2 appeared to be didehydrohalogenation of the 1,4-dihalide of 2,2*a*,3,4-tetrahydro-1*H*-cyclopent[*cd*]indene (5a). Attempts at bromination of the 1-chloro^{2b} or 1-bromo compounds (5b or 5c) with *N*-bromosuccinimide followed, or accompanied, by didehydrobromination¹⁰ were unsuccessful, but indicated spontaneous elimination of one hydrogen halide moiety to give an unstable olefin.

Accordingly, attention was directed toward a synthesis of 2,2*a*-dihydro-1*H*-cyclopent[*cd*]indene (6) and a study of its properties. The alcohol 5f was recovered



quantitatively from an attempted dehydration *via* treatment of its tosylate in pyridine. Heating the bromide 5c with potassium *tert*-butoxide in refluxing

- (9) A. Streitwieser, Jr., *Tetrahedron Lett.*, 23 (1960), and personal communication.
 (10) R. A. Barnes, *J. Amer. Chem. Soc.*, **70**, 145 (1948).

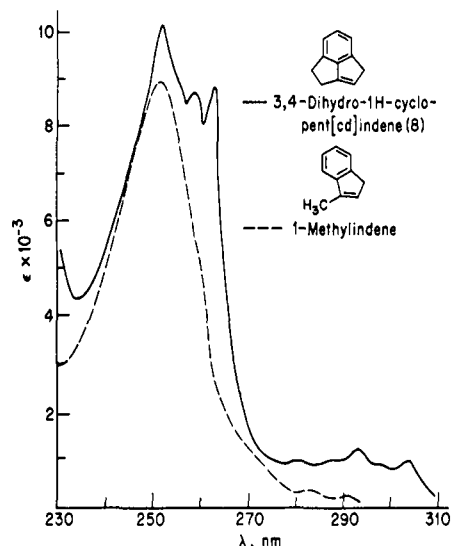


Figure 1.—Ultraviolet spectra in ethanol of 3,4-dihydro-1*H*-cyclopent[*cd*]indene (**8**) and 1-methylindene.

tert-butyl alcohol gave olefinic material as shown by the ultraviolet absorption of the product, but the isolated material had the composition $C_{11}H_{10}O$.

Elimination from the quaternary amine hydroxide was next investigated. The ketone **7** was converted in excellent yield by a Leuckart reaction¹¹ to the dimethylamine **5d**, which gave a crystalline methiodide. Pyrolysis of the corresponding quaternary hydroxide gave a 75% yield of a colorless, crystalline compound, $C_{11}H_{10}$, mp 40–44°, with the same ultraviolet absorption as observed in the dehydrobromination experiment. On several hours' exposure to air, this crystalline material turned to a slightly yellow oil identical with the monooxygenated compound obtained from the *tert*-butoxide reaction above.

The $C_{11}H_{10}$ olefin was sensitive to acid, but could be stored indefinitely without change under nitrogen at -15° . Its nmr spectrum showed only one vinyl proton, establishing that the compound was not the expected olefin **6**, but the isomeric 3,4-dihydro-1*H*-cyclopent[*cd*]indene (**8**). The same olefin was obtained from pyrolysis of the *N*-oxide **5e** and pyrolysis of the acetate **5g**, even though both procedures^{12,13} generally give little or no isomerization. The ultraviolet absorption of **8** is similar to that of 1-methylindene¹⁴ (Figure 1) but does not show the expected decrease in extinction coefficient and smoothing out of fine structure, as does, for example, **5a**, when compared to an unstrained model compound.^{2a} Evidently, effects other than simple strain are involved, probably involving interaction of the π electrons of the benzene ring and the double bond.

Dehydrobromination was again attempted as a method for introducing the second olefinic bond. A crystalline monobromo compound was obtained from the reaction of olefin **8** with *N*-bromosuccinimide, but it could not be dehydrobrominated. Nmr revealed that the compound was 2-bromo-3,4-dihydro-1*H*-cy-

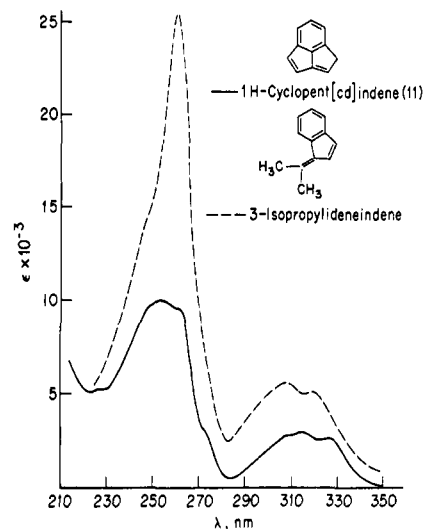
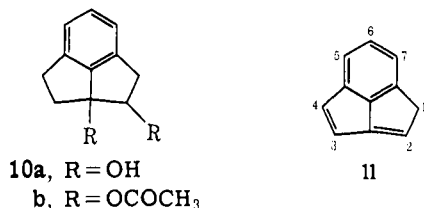


Figure 2.—Ultraviolet spectra in ethanol of 1*H*-cyclopent[*cd*]indene (**11**) and 3-isopropylideneindene.

clopent[*cd*]indene (**9**), the result of an unusual vinylic bromination. There was no vinyl proton absorption, and the rest of the spectrum was essentially the same as that of **8**.

A diolefin was finally obtained by the convenient acetate cracking procedure. Preparation of the diol **10a** by reaction of olefin **8** with osmium tetroxide and



its subsequent conversion to the diacetate **10b** went smoothly and in good yield. The diolefin, 1*H*-cyclopent[*cd*]indene (**11**), was isolated as an oil. Its ultraviolet spectrum corresponds well to that of 3-isopropylideneindene,¹⁵ taking into account the expected bathochromic shift and decreased extinction coefficient² (Figure 2). Its nmr spectrum was in accord with the indicated structure (Figure 3). Diolefin **11** is sensitive to oxygen, but may be stored under nitrogen at -15° indefinitely.

When fluoradene is treated with sodium methoxide in methanol, an immediate change occurs^{3a} in the ultraviolet absorption, indicating anion formation. Diolefin **11** was not expected to be as acidic as fluoradene and this was confirmed when no change occurred in its uv spectrum upon addition of methoxide (methanol) or isopropoxide (isopropyl alcohol). However, when 1*H*-cyclopent[*cd*]indene (**11**) was treated with potassium *tert*-butoxide in *tert*-butyl alcohol a gradual destruction of the spectrum occurred over 5 min, indicating that the pK_a is greater than 18–20.

Several attempts were made to convert **11** to the desired isomeric diolefin **2**. The anion of **11** was prepared under argon with potassium *tert*-butoxide in dimethyl sulfoxide¹⁶ and quenched with D_2O . Since the

(11) M. L. Moore in "Organic Reactions," Vol. V, Wiley, New York, N. Y., 1949, p 301.

(12) A. C. Cope, E. Czaneck, and N. A. LeBel, *J. Amer. Chem. Soc.*, **81**, 2799 (1959).

(13) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(14) P. Ramart and M. H. Hoch, *Bull. Soc. Chim. Fr.*, **5**, 848 (1938).

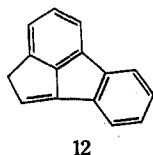
(15) A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, Y. Hirshberg, and Y. Sprinzak, *ibid.*, **18**, 702 (1951).

(16) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfeld, *J. Amer. Chem. Soc.*, **83**, 3678 (1961).

charge density on C-2a is calculated to be greater than on C-1,^{5,9} rate-controlled protonation should give 2-2a-d. Instead, only 11-1-d, as determined by nmr (Figure 3), was recovered, even when the anion was quenched with D₂O containing a slight excess of *p*-toluenesulfonic acid. It was not possible to distinguish whether only 11-1-d was formed initially, or whether deuteration took place to give 2-2a-d followed by isomerization to 11-1-d. If the latter were the case, then 2 would be strongly acidic, as predicted. It is also possible that deuteration occurred on the central carbon, C-7b, followed by isomerization. Calculations⁹ indicate that the compound so formed (ΔM 2.314) would not be as acidic as 2 (ΔM 2.411), but more acidic than 11 (ΔM 1.924).

It is evident that 2, if capable of existence, would have to be synthesized by a totally different route designed to prevent the ready isomerization of the double bonds.¹⁷

9bH-Cyclopenta[*jk*]fluorene (3).—The monodebenzo analog of fluoradene was prepared by the reaction of 2,9b-dihydro-1H-cyclopenta[*jk*]fluorene (4) and *N*-bromosuccinimide followed by spontaneous elimination of hydrogen bromide. The crude reaction mixture also contained 2H-cyclopenta[*jk*]fluorene (12), nmr



easily distinguishing between the two isomers and integration indicating that the mixture was 70–80% 3. The nmr spectrum of the mixture remained the same whether the carbon tetrachloride solution was washed with H₂O, D₂O, aqueous bicarbonate, or aqueous hydrochloric acid, or if hydrogen bromide or deuterium bromide were bubbled through the refluxing carbon tetrachloride solution. These experiments show that there is no equilibration between the isomers under either the reaction or work-up conditions, and therefore, the mixture must result from bromination occurring at the different positions (probably 2a and 9b) at similar rates.

The ultraviolet absorption of the mixture was not useful, since it did not resemble either the spectrum of 1,10b-dihydrofluoranthene or 2,3-dihydrofluoranthene.¹⁵ The mixture of 3 and 12 is extremely sensitive to oxygen, changing to an insoluble orange solid after a few seconds' exposure to air, even in carbon tetrachloride solution. Analysis of the material obtained on short-path distillation showed substantial oxygen incorporation, and the uv absorption of the distillate was quite different from that before distillation. The reaction mixture was also unstable to chromatography.

No change was observed in the uv spectrum of the mixture containing 3 when methanolic sodium methoxide was added; however, potassium *tert*-butoxide in *tert*-butyl alcohol caused immediate destruction of the spectrum, indicating that the pK_a lies between 16 and 20. Since the C-12 hydrogen of fluoradene is ex-

(17) A recent publication [P. Eilbracht and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, **10**, 751 (1971)] reports similar weak acidity for 1H-cyclopent[*cd*]indene (11) and similar properties for this compound prepared by a different method.

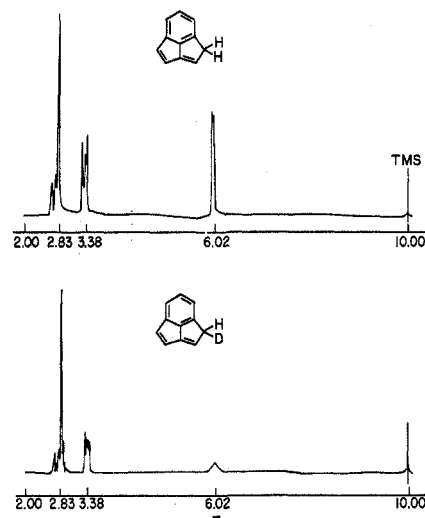


Figure 3.—Nuclear magnetic resonance spectra of 1H-cyclopent[*cd*]indene (11) and 1H-cyclopent[*cd*]indene-1-d.

changed for deuterium in refluxing deuterium ethoxide, a similar attempt was made to exchange the 9b hydrogen of 3, but total decomposition occurred. Some exchange took place in tritiated ethanol at room temperature, but the exchanged material was at least 400 times less active than fluoradene treated in the same manner.

These findings are clearly contrary to expectation. Probably the best explanation is that strain is not relieved to as great an extent as anticipated, so that the difference in resonance stabilization between the hydrocarbon and the anion is not as large in 3 as in fluoradene. There might be other factors that come into play in this unusual system, such as spatial interaction of the π system and steric inhibition of resonance, that are difficult to predict and whose magnitude would be difficult to estimate. It must also be borne in mind that MO calculations on nonalternant hydrocarbons give only rough estimates of their properties, and, therefore, the lack of agreement in the present case may not be too surprising.

It is interesting to note that structure 3 was postulated by Goldschmidt in 1880 as the structure of fluoranthene, whose relationship to fluorene was quickly established by oxidation experiments. The original analyses for fluoranthene were low in carbon, leading to a C₁₅H₁₀ formulation.¹⁸ The situation was resolved by von Braun, who thought structure 3 was untenable on theoretical grounds, and synthesized the correct structure for fluoranthene.¹⁹

Experimental Section²⁰

1-Bromo-2,2a,3,4-tetrahydro-1H-cyclopent[*cd*]indene (5c).—The bromide 5c was prepared (88% yield) in the same manner as the chloride 5b,^{2b} substituting HBr for HCl.

Anal. Calcd for C₁₇H₁₁Br: C, 59.2; H, 4.9; Br, 35.8. Found: C, 58.9; H, 4.8; Br, 35.8.

(18) G. Goldschmidt, *Monatsh. Chem.*, **1**, 221 (1880), and references cited therein.

(19) J. von Braun and G. Manz, *Ber.*, **63**, 2608 (1930).

(20) Melting points were taken on a Kofler hot stage; microanalyses were by the Analytical Laboratory, Department of Chemistry, University of California, Berkeley. Ultraviolet spectra were taken in ethanol or methanol with a Cary Model 14 recording spectrophotometer and are reported in nanometers, and nuclear magnetic resonance spectra are reported as τ values and were taken in carbon tetrachloride with tetramethylsilane as internal standard using a Varian A-60 spectrometer, unless otherwise noted.

Attempted Dehydrobromination of 5c.—A solution prepared from 80 mg (2 mg-atoms) of potassium and 5 ml of *tert*-butyl alcohol was heated at reflux for 1 hr after addition of 446 mg (2 mmol) of 5c. The *tert*-butyl alcohol was evaporated, the residue was extracted into ether, and the ether was washed with 1 *N* HCl and 10% NaHCO₃. Short-path distillation (90°, 2 μ) gave 30 mg (10%) of a yellow oil, uv max 248 and 295 nm.

Anal. Calcd for C₁₁H₁₀O: C, 83.5; H, 6.4. Found: C, 83.1; H, 6.2.

1-Dimethylamino-2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (5d).—A mixture of 2.00 g (13 mmol) of ketone 7, 3.67 g (50 mol) of dimethylformamide, and 1 ml of 85% formic acid was heated at 175° in a flask fitted with a short air condenser. After 2 hr, an additional 2 ml of 85% formic acid was added and heating was continued overnight. The dark reaction mixture was diluted with three times its volume of 0.5 *N* HCl, washed with benzene, made alkaline with concentrated NaOH, and extracted four times with benzene. Evaporation of the combined benzene extracts and short-path distillation at 65° (5 mm) of the residue gave 1.81 g (76%) of the amine 5d as a colorless oil.

Anal. Calcd for C₁₄H₁₇N: C, 83.4; H, 9.1; N, 7.5. Found: C, 83.2; H, 9.3; N, 7.2.

The methiodide of 5d was prepared with methyl iodide in methanol and was recrystallized from absolute ethanol, mp 205°.

Anal. Calcd for C₁₄H₂₀NI: C, 51.1; H, 6.1. Found: C, 51.4; H, 6.2.

3,4-Dihydro-1H-cyclopent[cd]indene (8).—Silver oxide, freshly prepared from 0.89 g (22 mmol) of sodium hydroxide and 1.90 g (11 mmol) of silver nitrate, was added to a warm solution of 1.00 g of 5d methiodide in 25 ml of CO₂-free water. The grey suspension was shaken for several hours and filtered, and most of the water was evaporated. Distillation was continued in an oil bath at 200° under a stream of nitrogen until decomposition was complete. Water was added in three separate portions to complete steam distillation of the product, which was dissolved in ether. The ether solution was washed with pH 4.5 phosphate buffer and bicarbonate, and evaporated under a stream of nitrogen. Sublimation at 50° (10 mm) gave 0.32 g (75%) of colorless crystals of olefin 8: mp 40–44°; uv max 252 nm (ε 10,100), 259 (8700), 263 (8700), 281 (960), 293 (1200), 304 (970); nmr τ 3.10 (3, ArH), 4.44 (t, 1, =CH), 6.47 (m, 4, ArCH₂), 7.13 (t, 2, ArCH₂CH₂C=).

Anal. Calcd for C₁₁H₁₀: C, 92.9; H, 7.1. Found: C, 92.6; H, 7.0.

The olefin 8 also was prepared by pyrolysis of *N*-oxide 5e. To an ice-cooled solution of 270 mg (1.45 mmol) of amine 5d in 7 ml of ether was added 18 ml of a 0.4 *M* ethereal solution of monophtalic acid (7.2 mmol). A gum precipitated immediately which dissolved slowly when the solution was warmed to room temperature and 10 ml of saturated NaHCO₃ was added. The ether was washed with saturated NaHCO₃ and the combined bicarbonate washes were extracted exhaustively with chloroform to give 270 mg of yellow oil on evaporation. This oil was sublimed at 70–90° (25–35 mm), giving 110 mg (53%) of olefin 8.

The same olefin 8 was obtained by pyrolysis of 1-acetoxy-2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (5g). The alcohol 5f^{2a} (540 mg, 3.4 mmol) was heated with 1 ml of acetic anhydride in 10 ml of pyridine at reflux for 4 hr. Evaporation of the reaction mixture left an oil, which was dissolved in benzene and passed through a tube, packed with glass helices, at 480° in a slow stream of nitrogen. The eluent was collected in a Dry Ice-acetone cooled trap. The contents of the trap were washed into benzene, the benzene solution was washed with water, dried, and evaporated, and the residue was sublimed at 50° (10 mm) to give 360 mg (75%) of crystalline olefin 8.

2-Bromo-3,4-dihydro-1H-cyclopent[cd]indene (9).—A mixture of 260 mg (1.5 mmol) of *N*-bromosuccinimide and 210 mg (1.5 mmol) of olefin 8 in 5 ml of carbon tetrachloride was heated at reflux overnight under nitrogen. Ether was added, the solution was washed with water and 5% NaHCO₃, the ether was evaporated, and the residue was sublimed at 70° (10 mm) to give 220 mg (67%) of yellow crystals of vinyl bromide 9 melting around room temperature: uv max 261, 270, 297, 308 nm; nmr τ 3.1 (3, ArH), 6.3 (2, ArCH₂C=), 6.6 (2, ArCH₂-), 7.2 (2, ArCH₂CH₂C=).

Anal. Calcd for C₁₁H₉Br: C, 59.7; H, 4.5; Br, 35.8. Found: C, 59.4; H, 4.8; Br, 35.9.

2,2a-Dihydroxy-2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (10a).—A mixture of 690 mg (2.3 mmol) of osmium tetroxide and 320 mg (2.2 mmol) of olefin 8 in 6 ml of ether and 5 drops of pyridine was kept at room temperature for 18 hr, and then poured

into a solution of 10.5 g of sodium sulfite and 8.7 g of sodium bicarbonate in 120 ml of water layered with 50 ml of benzene and 60 ml of methanol. The whole was shaken for several hours, and the brick-red precipitate was removed using Celite, the precipitate was washed with a small amount of methanol-benzene, and the benzene phase was removed. The aqueous layer was stripped of methanol and extracted with chloroform. The oily residue from evaporation of the combined benzene and chloroform layers was treated with a small amount of benzene and the resulting crystals were sublimed at 100° (1 mm) and recrystallized from benzene to give 330 mg (85%) of diol 10a, mp 139–140°.

Anal. Calcd for C₁₁H₁₂O₂: C, 75.0; H, 6.8. Found: C, 75.0; H, 7.0.

2,2a-Diacetoxy-2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (10b).—A solution of 90 mg (0.5 mmol) of diol 10a in 0.2 ml of acetic anhydride and 2 ml of pyridine was heated at reflux under nitrogen for 4 hr. Ether and water were added, and the ether layer was washed with 1 *N* HCl and 5% NaHCO₃, dried, and evaporated. Short-path distillation at 80° (1 mm) of the residue gave 110 mg (85%) of the diacetate 10b as a slightly yellow oil, nmr τ 8.02, 8.04 (2 s, 6, CH₃CO-), 4.78 (q, 1, >CHOCO-).

Anal. Calcd for C₁₅H₁₆O₄: C, 69.2; H, 6.2. Found: C, 69.6; H, 6.3.

1H-Cyclopent[cd]indene (11).—Crude diacetate 10b, prepared from 60 mg (0.34 mmol) of diol 10a, was dissolved in a small amount of benzene and passed through a 20-cm tube, packed with glass helices, at 480° in a slow stream of nitrogen. The pyrolysate was collected in a Dry Ice-acetone cooled trap and taken up in ether, and the ether was washed with water, dried, and evaporated. The residue was distilled (45°, 2.5 mm) onto a cold finger to give 25 mg (52% based on diol 10a) of diolefin 11 as a slightly yellow oil: uv max 252 nm (ε 10,000), 315 (3400), 327 (2800); nmr τ 6.02 (d, 2, *J* = 1.6 Hz, -CH₂-), 3.35 (t, 2, -CH=CH-), 2.6–3.0 (4, HC=, ArH).¹⁷

Anal. Calcd for C₁₁H₈: C, 94.3; H, 5.7. Found: C, 94.1; H, 5.9.

Attempted Preparation of 2aH-Cyclopent[cd]indene (2).—Diolefin 11 was dissolved in 0.5 ml of dimethyl sulfoxide (dried over molecular sieves) and added through a serum cap to excess sublimed potassium *tert*-butoxide in 0.5 ml of DMSO under argon in a closed flask. The resulting dark red solution was immediately syringed out and added to 7 ml of D₂O. Carbon tetrachloride was added and argon was bubbled through the mixture. The carbon tetrachloride solution was withdrawn into a syringe, filtered through MgSO₄, and evaporated in a stream of helium to a small volume in an nmr tube. The process was repeated in a second experiment with D₂O containing a slight excess of deuterium-exchanged *p*-toluenesulfonic acid, with the same results: uv max same as diolefin 11; nmr τ 6.00 (broad, -CHD-), 3.35 (t, 2, -CH=CH-), 2.6–3.0 (4, HC=, ArH).

9bH-Cyclopenta[*jk*]fluorene (3).—2,9b-Dihydro-1H-cyclopenta[*jk*]fluorene (4), 38.3 mg (0.2 mmol), was dissolved in 1 ml of carbon tetrachloride, and 35.6 mg (0.2 mmol) of *N*-bromosuccinimide was added. The mixture was heated on a steam bath for 20 min under nitrogen as hydrogen bromide was evolved. The cooled mixture was filtered, the filtrate was evaporated to ca. 0.3 ml, and the nmr spectrum was taken. Alternatively, H₂O or D₂O was added as nitrogen was bubbled through, the carbon tetrachloride layer was withdrawn with a syringe, filtered through MgSO₄, and evaporated, or the solution was washed with 10% NaHCO₃ or with 0.5 *N* HCl or refluxed with additional *N*-bromosuccinimide, HBr, or DBr. From all procedures, short-path distillation at 70° (3 mm) gave the same yellow oil, which was about a 3:1 mixture of 9bH-cyclopenta[*jk*]fluorene (3) and 2H-cyclopenta[*jk*]fluorene (12): nmr of 3, τ 4.84 (d, 1, *J* = 4 Hz, ArCH=C), 5.68 (q, 1, *J* = 16, 4 Hz, ArC=CH), 6.83 (d, 1, *J* = 16 Hz, ArCH); nmr of 12, τ 3.42 (t, 1, CH₂CH=), 6.08 (d, 2, ArCH₂).

Tritium Exchange Studies with Fluoradene (1) and 9bH-Cyclopenta[*jk*]fluorene (3).—Fluoradene (1) (12 mg) was dissolved in 5 ml of tritiated ethanol (200 μCi/ml) and the solution was allowed to sit at room temperature for 48 hr. The solvent then was removed under high vacuum and the residue was sublimed, giving recovered fluoradene (1) with an average count of 6.6 × 10⁶ dpm/mmol.

The same procedure applied to the 9bH-cyclopenta[*jk*]fluorene (3) prepared above gave recovered material with an average count of 1.6 × 10⁴ dpm/mmol.

1,10b-Dihydrofluoranthene.—3-Oxo-1,2,3,10b-tetrahydrofluoranthene^{2c} (60 mg, 0.33 mmol) in 2 ml of methanol was re-

duced with 1 g of sodium borohydride in 2 ml of 50% aqueous methanol. Addition of water precipitated 3-oxy-1,2,3,10b-tetrahydrofluoranthene, which after sublimation (100°, 0.5 mm) had mp 112° (lit.²¹ mp 130–134° for the alcohol obtained by reduction of the ketone with sodium amalgam).

Anal. Calcd for C₁₆H₁₄O: C, 86.5; H, 6.3. Found: C, 86.2; H, 6.2.

The alcohol was heated under reflux with 2 ml of pyridine and 0.5 ml of acetic anhydride for 15 hr, after which water and ether were added. After the ether phase was washed with 1 N HCl and 5% NaHCO₃, it was dried and evaporated to yield crude acetate, which was dissolved in toluene and passed through a packed tube at 470°. The pyrolysate was washed from the Dry

(21) J. von Braun and G. Manz, *Justus Liebigs Ann. Chem.*, **488**, 111 (1931).

Ice-acetone cooled trap with toluene, the toluene was evaporated, and the residue was crystallized from ethanol and then sublimed at 60° (1 mm) to give 1,10b-dihydrofluoranthene: mp 78–79°; uv max 235 nm (ε 18,900), 267 (21,000), 275 (20,700), 286 (18,500) 311 (3000), 323 (3400), 341 (2300), 357 (2300); nmr τ 6.13 (q, 1, Ar₂CH), 3.93 (m, 1, ArC=CH), 3.45 (d, 1, ArCH=C).

Anal. Calcd for C₁₆H₁₂: C, 94.1; H, 5.9. Found: C, 93.8; H, 6.1.

Registry No.—1, 205-94-7; 3, 35324-19-7; 5c, 35324-20-0; 5d, 35324-21-1; 5d MeI, 35324-22-2; 8, 14310-97-5; 9, 35324-24-4; 10a, 35324-25-5; 10b, 35324-26-6; 11, 209-69-8; 12, 208-69-5; 3-oxy-1,2,3,10b-tetrahydrofluoranthene, 35324-28-8; 1,10b-dihydrofluoranthene, 35324-29-9.

β-Carbonylamides in Peptide Chemistry. β-Aminoenones and β-Aminoenediones from N-Acetoacetyl Derivatives of Secondary Amino Acids

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A comparative study on the behavior of some N-acetoacetyl (AcA) derivatives of secondary amino acids with dicyclohexylcarbodiimide was made. N-Methyl-AcA-amino acids yield 2-acetylideneoxazolidin-5-ones (6), whose stereochemistry and condensation with nucleophiles are reported. N-AcA-Proline, in turn, forms a bicyclic azlactone (7) and a tetramic derivative (8); the latter reacts with nucleophiles yielding diastereomeric β-aminoenediones (10, 10') stabilized through hydrogen bonding.

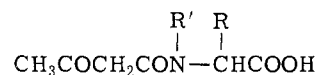
During previous research¹ on the reactions of N-acetoacetyl amino acids (AcA-aa, 1) with dicyclohexylcarbodiimide (DCCI) we obtained 2-acetylideneoxazolidin-5-ones 3, which behave as possible intermediates in the condensation with nucleophiles; in some cases, we observed a condensation-racemization ratio more favorable than known for 2-oxazolin-5-ones (4, X = O), which racemize through enolates or mesoionic species.²

A 2-acetyloxazoline structure (4, R'' = CH₂C(OCH₃), X = R₂ or RH), tautomerically related to 3, was recently proposed, in turn, for the transformation products of pertinent acetoacetamides.³

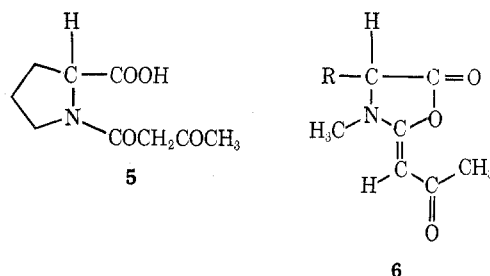
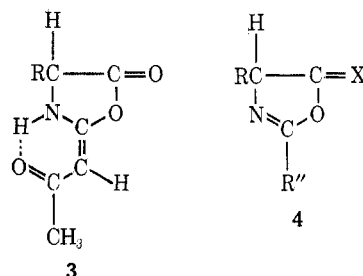
In this paper we report on the behavior of AcA derivatives of N-methylamino acids and proline in the presence of the same activator of the carboxyl groups, namely DCCI. Furthermore, we studied how the eventual formation of oxazole derivatives would affect the retention of configuration in the condensation reaction.

N-Methyl-AcA-aa (2) condenses with amino acid esters in the presence of DCCI to give racemized N-methyl-AcA dipeptides. On the other hand, when 2 is treated with DCCI in the absence of nucleophiles, the very reactive 2-acetylidene-3-methyloxazolidin-5-ones (6) are obtained in almost quantitative yields. Structure 6 is supported by strong carbonyl absorption at 1840 cm⁻¹, β-aminoenone maximum near 275 nm (ε >20,000),⁴ and the presence of singlets for the vinyl proton and the CH₃CO group at δ 4.8 and 2.3, respec-

tively. The hypsochromic-hyperchromic shift of the uv maximum and the strong shift of the vinyl proton with respect to the chelated structures 3 [uv max 285



- 1, R' = H
2, R' = CH₃



(1) C. Di Bello, F. Filira, and F. D'Angeli, *J. Org. Chem.*, **36**, 1818 (1971), and references cited therein.

(2) Cf. M. Goodman and C. Glaser in "Peptides, Chemistry and Biochemistry," B. Weinstein and S. Lande, Ed., Marcel Dekker, New York, N. Y., 1970.

(3) T. Kato and M. Sato, *Chem. Pharm. Bull.*, **17**, 2405 (1969); T. Kato, Y. Yamamoto, and M. Sato, *Yakugaku Zasshi*, **91**, 384 (1971).

(4) D. L. Ostercamp, *J. Org. Chem.*, **35**, 1632 (1970).

nm (ε ca. 12,000); =CH at δ 5.2],¹ confirm that the present compounds have the thermodynamically favored trans configuration 6. In no reaction could the alternative diastereomer be detected. This contrasts with the related β-aminoalkenoates and β-aminoenones, which are obtained under proper conditions as cis-