drous hydrogen chloride to give 1.2 g. (5.0%) of diphenylamine hydrochloride, m.p. 169–172° with decomposition; m.p. of the free base, 55–56° alone and when mixed with an authentic sample. Distillation of extract 2 gave 2.1 g. (9.0%) of aniline, b.p. 87–89° at 30 mm., N-benzoyl derivative, m.p. 160–161° (from 95% ethanol) alone and when mixed with an authentic sample.

In those reactions which were performed by the one-flask method all of the sodium amide was prepared in one flask and then the reactions were effected as described above.

Preparation of an Authentic Sample of 3-Phenyl-2-pentanone. (a) **Synthesis of α-Phenylbutyronitrile.**—Phenylacetonitrile (1.5 moles, 176.0 g.) was added over a period of 2.5 hours to sodium amide (1.5 moles) suspended in 1500 ml. of liquid ammonia. The ammonia was replaced by anhydrous ether. Then diethyl sulfate (1.5 moles, 231.5 g.) was added over a 2-hour period and the mixture was allowed to stand overnight. It was then poured onto ice and was extracted with several portions of ether. The combined extracts were dried over anhydrous sodium sulfate and distilled to give 37.6 g. of recovered phenylacetonitrile, b.p. 86–93° at 5.6 mm., and 152.5 g. (70.0%) of α-phenylbutyronitrile, b.p. 103–105° at 6.4 mm. (lit. value 88–93° at 5.0 mm.).[12]

(b) **Hydrolysis of α-Phenylbutyronitrile to α-Phenylbutyric Acid.**—The nitrile was hydrolyzed in 53.0% yield to α-phenylbutyric acid, b.p. 124–126.5° at 1.7 mm. (lit.[9] value 138° at 4 mm.) using the method described in the literature[9] for the hydrolysis of similar nitriles.

(c) **Conversion of α-Phenylbutyric Acid to 3-Phenyl-2-pentanone.**—α-Phenylbutyric acid (0.1 mole, 16.4 g.), dissolved in an equal volume of anhydrous ether, was added over a period of 1.5 hours to methyllithium (0.3 mole) in 300 ml. of anhydrous ether. The mixture was refluxed for 0.5 hour, poured onto ice, extracted with ether and the basic ether extracts discarded. The reaction mixture was then acidified with dilute hydrochloric acid and extracted with several portions of ether. The combined extracts were dried over anhydrous sodium sulfate and distilled to give 13.5 g. (83.0%) of 3-phenyl-2-pentanone, b.p. 81–85° at 4 mm.[9]; semicarbazone,[11] m.p. 188.8–189.8°.

Attempted Cleavage of Desoxybenzoin. (a) **By Sodioaniline.**—Desoxybenzoin (0.06 mole, 11.8 g.) was added as the solid to sodioaniline (0.12 mole), which was prepared from sodium amide (0.12 mole) and aniline (0.12 mole, 11.2 g.) in 300 ml. of liquid ammonia. The reaction mixture was stirred for 10 minutes and then processed in the regular manner to give 10.9 g. (92.0%) of recovered desoxybenzoin, m.p. 56.5–57.5°, and 9.3 g. (83.0%) of recovered aniline, b.p. 94–96° at 39.1 mm.; N-benzoyl derivative, m.p. 160–161° alone and when mixed with an authentic sample.

(b) **By Sodium Amide.**—When the last reaction was repeated except that desoxybenzoin (0.1 mole, 19.6 g.) was added to sodium amide (0.2 mole) in 400 ml. of liquid ammonia there was obtained 18.5 g. (94.5%) of recovered desoxybenzoin, m.p. 56.8–57.4°.

Attempted Cleavage of Phenyl Benzhydryl Ketone by Sodium Amide.—Phenyl benzhydryl ketone (0.02 mole, 5.4 g.), prepared by the method of Yost and Hauser,[13] was added to sodium amide (0.04 mole) in 300 ml. of liquid ammonia. The mixture was stirred for 25 minutes and processed to give 4.9 g. (91.0%) of recovered phenyl benzhydryl ketone, m.p. 135.0–135.8°.[13]

Cleavage of Phenyl Trityl Ketone by Sodium Amide.—Phenyl trityl ketone (0.017 mole, 6.0 g.) was added to sodium amide (0.035 mole) in 300 ml. of liquid ammonia. The mixture was stirred for 25 minutes and processed to give 2.3 g. (38.3%) of recovered phenyl trityl ketone, m.p. 177–178°[14]; 1.1 g. (25.8%) of triphenylmethane, m.p. 92.6–93.6° alone and when mixed with an authentic sample; and 0.7 g. (34.0%) of benzamide, m.p. 126–127.4° alone and when mixed with an authentic sample.

Attempted Phenylation of Benzamide with Bromobenzene.—Benzamide (0.5 mole, 60.6 g.) was added to sodium amide (0.5 mole) in 1000 ml. of liquid ammonia. The mixture was stirred for 15 minutes. Then, bromobenzene (0.25 mole, 39.3 g.) was added and stirring was continued for an additional 5 minutes. Finally, sodium amide (0.5 mole in 350 ml. of liquid ammonia) was siphoned into the mixture from a second flask, stirring was continued for an additional 10 minutes and then the reaction mixture was processed to give: 59.7 g. (98.5%) of recovered benzamide, m.p. 126–127°; 4.2 g. (18.0%) of aniline, b.p. 103–105° at 60.7 mm.; 6.3 g. (30.0%) of diphenylamine, m.p. 55–56° alone and when mixed with an authentic sample; and 4.1 g. (20.0%) of triphenylamine, m.p. 126–127° alone and when mixed with an authentic sample.

(12) J. V. Murray and J. B. Cloke, THIS JOURNAL, **68**, 126 (1946).

(13) R. S. Yost and C. R. Hauser, *ibid.*, **69**, 2325 (1947).

(14) W. E. Bachmann, *Org. Syntheses*, **14**, 12 (1934).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Epoxyethers. XVIII. Reactions of α-Hydroxyacylals with Amines

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An α-hydroxyacylal II was isolated in good yield from the reaction of 1,2-epoxy-1-methoxy-2-methylpropane with 9-fluorenecarboxylic acid. This α-hydroxyacylal II reacted with triethylamine and piperidine to give a β-hydroxy-γ-lactone IV, with cyclohexylamine to give a β-(N-cyclohexyl)-amino-γ-lactone VI, and with ammonia to give 9-fluorenecarboxylic acid amide. The β-hydroxy-γ-lactone IV could be converted to the β-(N-cyclohexyl)-amino-γ-lactone VI.

The reactions of organic acids with isobutyraldehyde epoxyether have been shown previously to give relatively stable α-hydroxyacylals. These acylals readily underwent O-to-O acyl migrations in the presence of triethylamine catalyst with the loss of alcohol to give esters of α-hydroxyisobutyraldehyde.[3] Since the acylals are potential acylating agents, the object of the present work was to investigate the reaction of an α-hydroxyacylal with ammonia, a primary and a secondary amine. An α-hydroxyacylal from 9-fluorenecarboxylic acid was chosen so that the various products would be crystalline and the results indicated that the acylal would acylate only ammonia. The primary amine was incorporated into the product VI and the secondary amine gave the same product as a tertiary amine. In this instance product IV was not an ester of an α-hydroxyaldehyde III, resulting from O→O acyl migration, but rather the result of an additional internal aldol reaction.

When 9-fluorenecarboxylic acid was allowed to react with the epoxyether from isobutyraldehyde I at 0°, a solid acylal II resulted in over 90% yield.

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(2) Abstracted from the dissertation submitted by Bradley L. Winch in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Wayne State University, 1958.

(3) C. L. Stevens and B. T. Gillis, THIS JOURNAL, **79**, 3448 (1957).

Elemental and spectral analysis supported the assignment of an α-hydroxyacylal structure to II. An ether solution of this acylal reacted readily with an ether solution of ammonia to give 95% yield of 9-fluorenecarboxamide.

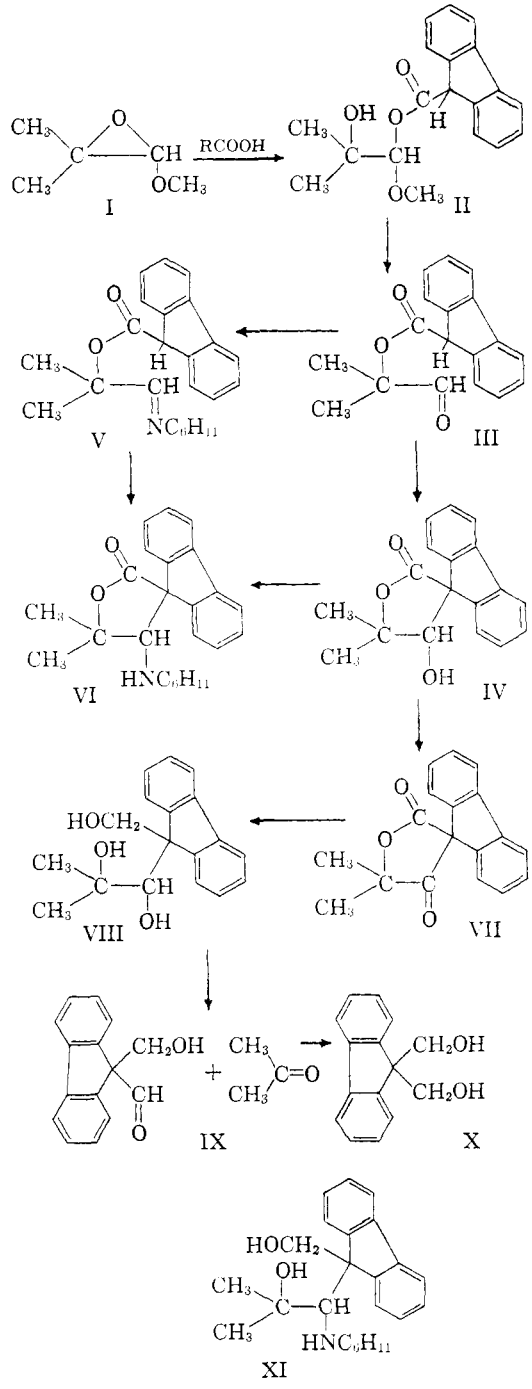
Treatment of the α-hydroxyacylal II with triethylamine in ether solution resulted in the formation of a product with the loss of methanol. However, this product, although isomeric, was not the corresponding α-hydroxyaldehyde ester III as indicated by a definite hydroxyl absorption band in the infrared spectrum. The presence of the hydroxyl group was confirmed by the preparation of a *p*-nitrobenzoate derivative and was shown to be secondary by oxidation to the corresponding ketone VII. Failure to give a 2,4-dinitrophenylhydrazone indicated that the compound no longer contained a carbon atom in the acetal, hemiacetal or other carbonyl state of oxidation. The carbonyl absorption in the infrared spectrum (5.74 μ in Nujol mull, 5.63 μ in chloroform) indicated a γ-lactone and from these data it was possible to propose structure IV for the product.

Confirmation of the structure of IV was accomplished by the following reaction sequence. Lithium aluminum hydride reduction of IV or VII gave the triol VIII which, when subjected to sodium metaperiodate oxidation, gave acetone, identified as its 2,4-dinitrophenylhydrazone derivative, and the β-hydroxyaldehyde IX. The aldehyde, which might be expected to readily undergo a reverse aldol reaction, was not isolated, but instead was immediately reduced to the 1,3-dihydroxy compound X. This diol X, 9,9-fluorenedimethanol, was synthesized independently.

Although the α-hydroxyaldehyde ester III was not isolated, the most reasonable mechanism for the formation of IV would involve formation of III by O→O acyl migration followed by an internal aldol reaction under the influence of the amine catalyst.

The acylal II would not acylate the primary amine cyclohexylamine, but rather a new product was formed which incorporated the amine with the loss of the elements of methanol and water. The product was basic although the hydrochloride was water insoluble. The structure VI was proposed for this product since the infrared spectrum indicated a γ-lactone, no aldehyde group could be detected and an N–H band at 3.05 μ in the infrared spectrum replaced the OH band of IV. This structure was confirmed by conversion of the hydroxylactone IV to the aminolactone by reaction with thionyl chloride followed by treatment with cyclohexylamine. Lithium aluminum hydride reduction of VI gave the aminodiol XI which gave acetone upon periodate oxidation.

The mechanism for the formation of V is interesting. The hydroxylactone IV was shown not to be the intermediate since under the conditions of the reaction it could not be converted to the aminolactone VI. The mechanism proposed here involves the formation of the Schiff base V from the aldehyde intermediate followed by a reaction analogous to the internal aldol reaction of III. If a full Schiff base is necessary as in V, and not merely an aldehyde amine addition product, then a secondary amine should not be expected to give an aminolactone. In fact, piperidine is not incorporated into the product, but catalyzed the formations of the hydroxylactone IV in good yield.



Experimental

1-Methoxy-2-methylpropane-1,2-diol-1-(9-fluorenecarboxylate) (II).—To 2.04 g. (0.02 mole) of 1,2-epoxy-1-methoxyisobutane[3] (I) in anhydrous ether was added 4.20 g. (0.02 mole) 9-fluorenecarboxylic acid. The homogeneous reaction mixture was allowed to stand at room temperature for two hours, then extracted with sodium bicarbonate solution, dried over anhydrous sodium sulfate, and filtered. Removal of the ether in vacuum gave 6.01 g. (96%) of crude acylal, m.p. 95–98°. Recrystallization from ether–petro-

leum ether gave 5.61 g. (90%) of the pure α-hydroxyacylal II, m.p. 98–100°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.25; H, 6.73.

A 2,4-dinitrophenylhydrazone melted at 197–199° dec. and was identical in every respect with methacrolein 2,4-dinitrophenylhydrazone obtained from α-hydroxyisobutyraldehyde dimethyl acetal.

9-(1,2-Dihydroxy-2-methylpropyl)-9-fluorenecarboxylic Acid γ-Lactone (IV). Procedure I.—To 10 g. (0.032 mole) of II in 25 ml. of dry tetrahydrofuran was added a catalytic amount of triethylamine. The reaction mixture was then refluxed on a steam-bath overnight. Removal of the solvent and recrystallization of the resulting solid from ethanol–water gave 6.0 g. (67%) of the lactone IV, m.p. 198°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75; O, 17.10. Found: C, 76.79; H, 5.88; O, 16.98.

Procedure II.—A solution of 5 g. (0.016 mole) of the acylal II in 30 ml. dry diethyl Carbitol and 6 drops triethylamine was refluxed for 18 hours. The reflux condenser was washed down with 10 ml. of dry benzene and the solution distilled (up to 85°) into a solution of 2.97 g. (0.016 mole) of *p*-nitrobenzoyl chloride in 50 ml. of dry pyridine. The pyridine solution was then heated to boiling and poured on crushed ice. The solid obtained was filtered, dissolved in ether, the ether solution washed with saturated bicarbonate solution, dried over sodium sulfate, and evaporated to dryness. The resulting solid, 1.74 g. (60%), melted at 95–96°. A mixture melting point with an authentic sample of methyl *p*-nitrobenzoate (m.p. 96°) was undepressed.

The diethyl Carbitol solution was evaporated to dryness *in vacuo* leaving a solid which, after recrystallization from ethanol–water, gave 3.4 g. (76%) of the β-hydroxy lactone IV, m.p. 198–200°.

Procedure III.—To 1.0 g. (0.0032 mole) of the acylal II in 20 ml. of dry benzene was added 0.32 ml. (0.0032 mole) of piperidine. The resulting solution was refluxed for 6 hours and then evaporated to dryness *in vacuo*. Recrystallization of the gummy material was effected from acetone–hexane to give 0.59 g. (60%) of a solid compound, m.p. 198–199°. This solid was shown to be identical with the β-hydroxy-γ-lactone IV obtained by treatment of the acylal II with a catalytic amount of triethylamine.

The β-hydroxy lactone IV gave a negative Schiff test, a negative 2,4-dinitrophenylhydrazone test and gave a negative nitrogen test after sodium fusion. A molecular weight determination (Rast) on IV gave a value of 264 (calcd. 280) and showed the compound to be monomeric. No uptake of hydrogen occurred when IV was subjected to hydrogenation in 95% ethanol, using platinum oxide as catalyst.

9-(1,2-Dihydroxy-2-methylpropyl)-9-fluorenecarboxylic Acid γ-Lactone *p*-Nitrobenzoate.—To 1.35 g. (0.0072 mole) of *p*-nitrobenzoyl chloride dissolved in 10 ml. of pyridine was added 1.0 g. (0.0036 mole) of the β-hydroxy lactone IV, dissolved in an equal amount of pyridine. The reaction mixture was allowed to stand at room temperature overnight, heated on a hot-plate for one hour, then poured on ice. The solid precipitate was filtered, dissolved in chloroform, extracted three times with 10% hydrochloric acid solution and three times with saturated sodium bicarbonate solution. The chloroform solution was dried over anhydrous sodium sulfate, evaporated to dryness, and the gummy product recrystallized from chloroform–hexane to give 1.43 g. (92.5%) of the desired *p*-nitrobenzoate ester of IV, m.p. 195°.

Anal. Calcd. for $C_{25}H_{19}NO_6$: C, 69.93; H, 4.46; N, 3.26; O, 22.36. Found: C, 70.13; H, 4.34; N, 3.50; O, 22.78.

α-(1-Hydroxyisopropyl)-9,9-fluorenedimethanol (VIII).—To 0.28 g. of lithium aluminum hydride in 25 ml. of anhydrous ether was added 2.0 g. (0.0064 mole) of the β-hydroxy lactone IV in 25 ml. of anhydrous ether. The reaction mixture was stirred overnight and water was added in small amounts to decompose the excess lithium aluminum hydride. Diatomaceous earth was added to coagulate the precipitated aluminum oxide and the resulting solution was filtered. The ether and water layers were separated and the water layer was washed three times with ether. The ether washings were combined with the original ether solution, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness giving 1.58 g. (87%) of the desired triol VIII, m.p. 143–144°. Two recrystallizations from boiling water gave an analytical sample which melted at 145°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: 76.24, 75.87; H, 7.37, 7.07.

The triol VIII was also obtained by a lithium aluminum hydride reduction of the β-keto lactone VII according to the following procedure. To 0.2 g. of lithium aluminum hydride in 25 ml. of anhydrous ether was added dropwise 0.1 g. (0.00036 mole) of the β-keto lactone VII dissolved in a mixture of 25 ml. of anhydrous ether and 25 ml. of anhydrous benzene. The reaction mixture was stirred for 36 hours and then the excess lithium aluminum hydride was decomposed by slowly adding water. The precipitated aluminum oxide was filtered and the ether–benzene solution was concentrated to a volume of 10 ml. Pentane was added until the solution became cloudy and the triol crystallized in the form of fine needles, 0.075 g. (73%), m.p. 144–145°. A mixture melting point with the triol obtained by reduction of the β-hydroxy lactone IV was undepressed.

Sodium Periodate Oxidation of VIII.—To 0.2 g. (0.0007 mole) of the triol VIII dissolved in 15 ml. of methanol (the methanol had been distilled over 2,4-dinitrophenylhydrazine reagent) was added 15 ml. of 0.097 *N* sodium metaperiodate solution. The solution was allowed to stand at room temperature for 23 hours and then the low boiling components of the solution were distilled into an acidified methanolic solution of 2,4-dinitrophenylhydrazine. After 30 minutes of standing at room temperature, the solution was evaporated to dryness *in vacuo*, the dry residue dissolved in benzene and chromatographed over neutral deactivated alumina to give 0.15 g. (90%) of acetone 2,4-dinitrophenylhydrazone, m.p. 122–124°. A mixture melting point with an authentic sample of acetone 2,4-dinitrophenylhydrazone, m.p. 124°, was undepressed.

The periodate oxidation was repeated for the purpose of isolating the second fragment produced by the oxidation. To 0.4 g. (0.0014 mole) of the triol in 20 ml. of methanol was added 30 ml. of 0.0976 *N* sodium metaperiodate solution. The reaction mixture was allowed to stand at room temperature for two days, diluted with water and extracted with ether. The ether solution was dried over anhydrous sodium sulfate, filtered, and divided into two equal parts. To one of the ether solutions was added 0.07 g. of lithium aluminum hydride. The reaction mixture was stirred overnight and the excess lithium aluminum hydride was decomposed by the cautious addition of water. After filtration of the precipitated aluminum oxide, the ether solution was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. Recrystallization of the residue from methylene chloride–hexane gave 0.098 g. (62%) of crystalline 9,9-fluorenedimethanol (X), m.p. 142–143°. A mixture melting point with an authentic sample of 9,9-fluorenedimethanol was undepressed. An analytical sample, m.p. 144°, was prepared by two recrystallizations from toluene.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.52; H, 6.19.

9-Hydroxymethyl-9-fluorenecarboxylic Acid.—To 2.10 g. (0.01 mole) of 9-fluorenecarboxylic acid in 5 ml. of methanol was added 50 ml. of 10% sodium hydroxide solution and 25 ml. of 38% formalin solution. The mixture was allowed to stand at room temperature for two days, acidified with hydrochloric acid at 0°, and extracted with methylene chloride. The methylene chloride solution was washed three times with water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness giving 1.5 g. (63%) of the desired hydroxymethyl acid, m.p. 154–155°. An analytical sample, m.p. 157–158°, was prepared by two recrystallizations from chloroform.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.04. Found: C, 75.18; H, 5.23.

9,9-Fluorenedimethanol X. Procedure I.—An ether solution of 0.5 g. (0.0021 mole) of 9-hydroxymethyl-9-fluorenecarboxylic acid was added dropwise with stirring to an ether solution of 0.15 g. of lithium aluminum hydride. The mixture was stirred overnight, the excess lithium aluminum hydride decomposed by cautious addition of water, and the precipitated aluminum oxide filtered. The ether solution was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness giving 0.4 g. (86%) of the desired 9,9-fluorenedimethanol, m.p. 142–143°.

Procedure II.—A solution consisting of 2.0 g. (0.012 mole) of fluorene, 10 ml. of ethanol, 2.0 g. of potassium hydroxide and 20 ml. of 38% formalin solution was refluxed for 48 hours and then diluted with water to a volume of 200 ml. The solution was extracted three times with ether, the ether dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. Recrystallization of the remaining gummy residue gave 0.2 g. (7.4%) of the desired 9,9-fluorenedimethanol, m.p. 142–144°. A mixture melting point with the diol prepared by procedure I was undepressed.

9-(2-Hydroxy-2-methyl-1-oxopropyl)-9-fluorenecarboxylic Acid γ-Lactone VII.—Nitrogen was passed into an acetone solution of 1.2 g. (0.0042 mole) of the β-hydroxy lactone IV for 15 minutes, and then 1.06 ml. (0.0042 mole) of standard Jones reagent[4] was added. Magnetic stirring was employed to ensure thorough mixing of the reactants. Complete decolorization of the chromic acid took place in 5 minutes, but stirring was continued for an additional 10 minutes. The solution was diluted with distilled water to a volume of 800 ml. and allowed to stand overnight at room temperature. The precipitate that had formed was filtered, dried, and recrystallized from boiling benzene, giving 1.15 g. (98%) of the desired keto lactone VII, m.p. 218–220°.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07; O, 17.25. Found: C, 77.67; H, 5.15; O, 17.54.

Ammonolysis of II.—Dry gaseous ammonia was bubbled into an ether solution of 0.5 g. (0.0016 mole) of the acylal II for one hour. The resulting solution was allowed to stand overnight at room temperature. At the end of this time, a precipitate had formed which, after recrystallization from 95% ethanol, had m.p. 252–255°. The precipitate, 0.32 g. (95.5%), proved to be 9-fluorenecarboxylic acid amide. A mixture melting point with an authentic sample of 9-fluorenecarboxylic acid amide was undepressed.

α-Hydroxyisobutyraldehyde Dimethyl Acetal 9-Fluorenecarboxylate (III).—Twenty-five ml. of pyridine was cooled to 0° and 4.56 g. (0.02 mole) of fluorene-9-carboxylic acid chloride added. To the resulting purple solution was added 2.68 g. (0.02 mole) of α-hydroxyisobutyraldehyde dimethyl acetal. The solution was swirled gently, allowed to stand at room temperature overnight, and then poured on crushed ice. The resulting solid was filtered and then taken up in ether. The ether solution was washed first with saturated bicarbonate solution, then with saturated sodium chloride solution, filtered through sodium sulfate and evaporated to dryness. The solid thus obtained was taken up in acetone and treated with decolorizing carbon. Recrystallization from hot hexane gave 3.89 g. (60%) of solid α-ester dimethyl acetal, m.p. 89°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80; O, 19.60. Found: C, 73.77; H, 6.70; O, 19.30.

None of the attempts to selectively hydrolyze the acetal linkage of this α-ester dimethyl acetal were successful.

A 2,4-dinitrophenylhydrazone, prepared as described earlier, melted at 197–199° dec. and was identical in every respect with methacrolein 2,4-dinitrophenylhydrazone obtained from α-hydroxyisobutyraldehyde dimethyl acetal.

9-(1-Cyclohexylamine-2-hydroxy-2-methylpropyl)-9-fluorenecarboxylic Acid γ-Lactone (VI).—A solution of 2.30 g. (0.0074 mole) of the α-hydroxy acylal II in 20 ml. of anhydrous benzene and 0.92 ml. (0.0074 mole) of cyclohexylamine was refluxed for 6 hours. The solution was then evaporated to dryness *in vacuo* and the residue crystallized from acetone–hexane to give 1.91 g. (72%) of the β-cyclohexylamino lactone VI, m.p. 186–188°. An analytical sample, m.p. 188°, was prepared by three recrystallizations from acetone–hexane.

Anal. Calcd. for $C_{24}H_{27}NO_2$: C, 79.74; H, 7.53; N, 3.88; O, 8.85. Found: C, 79.66; H, 7.65; N, 3.59; O, 8.89.

The β-cyclohexylamino lactone VI gave a negative Schiff test, a negative Benedict test, and a negative 2,4-dinitrophenylhydrazone test. It was insoluble in saturated sodium bicarbonate solution and in 3 *N* hydrochloric acid solution, although it did give positive test for nitrogen upon sodium fusion. Anhydrous gaseous hydrogen chloride was bubbled into an ether solution containing 1.0 g. of VI. After a few minutes, a solid hydrochloride, m.p. 240° dec., precipitated.

Anal. Calcd. for $C_{24}H_{28}ClNO_2$: Cl, 8.91. Found: Cl, 9.14, 9.09.

The original amino lactone could be recovered by suspending the hydrochloride in benzene and extracting with saturated sodium bicarbonate solution, followed by evaporation of the benzene solution to dryness. The hydrochloride was insoluble in water.

A molecular weight determination (Rast) on VI showed the compound to be monomeric: calcd. 361, found 442.

9-(1-Cyclohexylamino-2-hydroxy-2-methylpropyl)-9-fluorenemethanol (XI).—A solution of 0.8 g. (0.0022 mole) of the β-cyclohexylamino lactone VI in 25 ml. of anhydrous benzene was added dropwise over a 4-hour period to a stirred ether solution of 0.15 g. of lithium aluminum hydride. The reaction mixture was allowed to stir overnight and the excess lithium aluminum hydride was decomposed by the addition of water to the ether–benzene solution. The aluminum oxide was filtered, washed three times with benzene, the combined ether–benzene solution dried over anhydrous sodium sulfate, filtered, and evaporated almost to dryness. Upon the addition of hexane, crystals of the desired diol XI, 0.4 g. (50%), m.p. 152°, formed. Recrystallization from methanol–water and from toluene–pentane furnished an analytical sample, m.p. 152°.

Anal. Calcd. for $C_{24}H_{31}NO_2$: C, 78.86; H, 8.55. Found: C, 78.64, 78.92; H, 8.54, 8.37.

Sodium Periodate Oxidation of XI.—Into a solution of 0.2 g. (0.00055 mole) of XI in 25 ml. of methanol (distilled from 2,4-dinitrophenylhydrazine) and 10 ml. of tetrahydrofuran was pipetted 15 ml. of 0.0976 *N* sodium metaperiodate solution. The reaction mixture was allowed to stand at room temperature for 42 hours and then the low boiling components of the solution were distilled into a solution of Brady reagent. The Brady solution was allowed to stand at room temperature overnight, evaporated to dryness *in vacuo*, the dry residue dissolved in benzene and chromatographed over neutral deactivated alumina to give 0.13 g. (23%) of acetone 2,4-dinitrophenylhydrazone, m.p. 122–124°. A mixture melting point with an authentic sample of acetone 2,4-dinitrophenylhydrazone, m.p. 124°, was undepressed.

The portion of the solution which had not distilled was diluted with water, extracted with ether, the ether solution dried over anhydrous sodium sulfate, filtered, and subjected to reduction with lithium aluminum hydride. Treatment of the reduction in the usual manner gave only some starting diol XI, m.p. 152°.

Conversion of IV to VI.—A solution of 0.6 g. (0.0021 mole) of IV in 15 ml. of dry benzene and 2 ml. of thionyl chloride was refluxed for 14 hours, evaporated to dryness, more benzene added, and the solution evaporated to dryness a second time to ensure removal of excess thionyl chloride. Fifteen ml. of benzene and 1 ml. of cyclohexylamine was added and the resulting solution was refluxed for 36 hours. The amine-hydrochloride which had precipitated was filtered and the benzene solution was washed three times with 10% hydrochloric acid solution.

The hydrochloric acid solution was made basic with sodium hydroxide and extracted three times with benzene. The benzene was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. Treatment of the resulting solid with decolorizing carbon and recrystallization from acetone–hexane gave 0.100 g. (49%) of the β-cyclohexylamino lactone VI, m.p. 186–188°. A mixture melting point with a sample of VI prepared by treatment of the α-hydroxy acylal II with cyclohexylamine was undepressed.

Treatment of the benzene solution in the usual manner resulted in the recovery of 0.44 g. (0.0016 mole) of the starting β-hydroxy lactone IV, m.p. 198°. A mixture melting point with an authentic sample of IV was undepressed.

DETROIT 2, MICH.

(4) K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).