ALIPHATIC CHEMISTRY OF FLUORENE PART VII. SPIROLACTONES¹

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ABSTRACT

A number of spirolactones have been prepared from fluorene-9-carboxylic acid, either by the halolactonization reaction or by alkylation of the methyl ester with hydroxyalkyl halides.

The ease with which methyl fluorene-9-carboxylate anion (Ia) reacts with a wide range of alkyl halides (1, 2, 3) prompted attempts to prepare 9-alkyl derivatives of the ester-hydrochloride (II), which has found use as an anti-spasmolytic agent (4) under the name Pavatrine (5, pp. 259–261). Attempts to alkylate the anion Ib or to effect trans esterification of methyl 9-alkylfluorene-9-carboxylates with sodium 2-diethylaminoethoxide gave only traces of the desired products, but led indirectly to the preparation of some spirolactones.



The reaction between 2,3-dihydroxypropyl chloride and either of the anions Ia or b gave the hydroxy- γ -lactone IIIb in good yield. The unsubstituted γ (IIIa) and δ (IVa) lactones were prepared similarly, by alkylating Ia with 2-bromoethanol and 3-chloropropanol,* respectively. The phenyl γ -lactone (IIIc) was obtained by reducing methyl 9- ω -phenacylfluorene-9-carboxylate (6) with sodium borohydride. The carbonyl stretching frequencies of chloroform solutions of these lactones and the related compound Va (7), isomeric with IIIa, agree well with the generally accepted values (8, pp. 159–160).

The hydroxylactone (IIIb) was first reported (3) as having the isomeric δ -structure (IVb), on the basis of the carbonyl stretching frequency of a sample prepared as a pressed potassium bromide disk. However, the infrared spectrum of a chloroform solution indicated the γ -lactone structure (IIIb), and this has been confirmed by reaction with thionyl chloride to give the chloro- γ -lactone (IIId) (cf. reactions of the hydroxylactones derived from stilbene-2-carboxylic acids (9)). The chlorolactone has also been prepared from 9-allylfluorene-9-carboxylic acid (below). Structure IIIb for the hydroxylactone is in accord with the preferred formation of γ - over δ -lactones in the sugar series (10, pp. 33-34) and the hydroxylactones of stilbene-2-carboxylic acids (11).

The abnormal differences in the carbonyl stretching frequencies of samples of IIIb prepared as a potassium bromide disk and as a solution in chloroform may be due to

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*Commercial 3-chloropropanol contained approximately 20% of an isomeric chlorohydrin which was eliminated by careful fractional distillation.

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Va, R = H, $\nu_{C=0}$ (mull) = 1772 cm⁻¹ Vb, R = Br, $\nu_{C=0}$ (mull) = 1795 cm⁻¹

VI, $\nu_{C=0}$ (CHCl₃) = 1777 cm⁻¹

isomerization brought about by the high pressures required for disk formation (12, pp. 297-298; for another example of an abnormally low carbonyl frequency in a KBr disk, see ref. 13). Consequently, the infrared data discussed later in this paper refer to solutions in chloroform.

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Reaction of the anion Ia with trans-2-bromocyclohexanol, cis-2-chlorocyclohexanol, or cyclohexene oxide gave the same lactone (VI). Since cyclohexene oxide is known to react with nucleophiles with inversion at one carbon atom (14, 15), the lactone must have the trans structure. The lactone is formed from trans-2-bromocyclohexanol by prior formation of cyclohexene oxide (15) and from cis-2-chlorocyclohexanol by displacement with inversion (cf. the acetates of the 2-chlorocyclohexanols (16)). The reaction between Ia and 2-chlorocyclohexanone failed, thwarting attempts to prepare the cis isomer of VI. Notwithstanding Westheimer's successful preparation of a hydroxy diester from cyclopentene oxide and diethyl malonate (14), the reaction between Ia and trans-2-bromocyclopentanol failed to give the desired product.

The halolactonization and related reactions have recently aroused considerable interest. Van Tamelen and Shamma (17) have suggested that the formation of iodolactones is of diagnostic value in determining the position of unsaturation in olefinic acids, and this technique has been found to be of some use (18, 19). The formation of halolactones has proved particularly useful in the bicyclo[221]heptene series (e.g. ref. 20). The mechanism has been examined by Bartlett (21), Craig (22, 23), Arnold and co-workers (24, 25, 26, 27), and, in some detail, by Berti (9, 11, 28, 29, 30, 31). It has been shown to be stereospecific (9) and much evidence suggests that a carbonium ion or related species is the essential intermediate. Since α,α -disubstituted allylacetic acids form halolactones particularly readily (9), the opportunity has been taken to examine some 9-alkenylfluorene-9-carboxylic acids. (For the method of preparation of the acids, see ref. 3.)

9-Allylfluorene-9-carboxylic acid has now been shown to form a chloro- γ -lactone (III*d*) as well as the corresponding bromo (25) and iodo (24) compounds (III*e* and *f*, respectively). 9-Crotylfluorene-9-carboxylic acid* has been found to yield mainly the bromo- γ -lactone (III*g*) together with a trace of the isomeric δ -lactone (IV*c*), not obtained pure. 9-Cinnamylfluorene-9-carboxylic acid gave only the bromo- δ -lactone (IV*d*), which decomposed surprisingly readily to 9-cinnamylidenefluorene. The reactions of the crotyl and cinnamyl acids, like those of *cis*- and *trans*-stilbene-2-carboxylic acids (9), are best interpreted as proceeding by way of the more stable carbonium ion. It had been the intention to test this conclusion by examining the reactions of para-substituted cinnamyl derivatives but insufficient time has curtailed the project. 9-Propargylfluorene-9-carboxylic acid gave the heavily substituted tribromo- γ -lactone (III*h*), which decomposed at its melting point with evolution of bromine.



*The structure of this acid was proved by hydrogenation of the methyl ester to the known (2) methyl 9-butylfluorene-9-carboxylate. This confirmation was necessary since crotyl bromide exists as an equilibrium mixture under normal conditions (32) and can give rise to 'abnormal products' by the S_N 2 mechanism (33).

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9-3'-Cyclohexenylfluorene-9-carboxylic acid gave a good yield of the bromo- γ -lactone (VII). The homologous 3'-cyclopentenyl acid gave only a moderate yield of the lactone (VIII) but, nevertheless, afforded an example of the formation of a derivative of bicyclo-[330]octane under mild conditions. By analogy with Berti's studies (9), the lactones must have the partial stereochemistry shown. The preparation of VIII can be compared with the formation of the highly strained halo- β -lactones from dimethylmaleic and fumaric acids (21).

The carbonyl stretching frequency of the bromolactone prepared from allyldiphenylacetic acid (22) is 1783 cm⁻¹, showing it to be the γ -lactone IX.



The infrared data in this paper show that introduction of halogen γ or δ to the carbonyl group of δ - and γ -lactones results in a shift of the carbonyl stretching frequency to higher frequencies, by 15–20 cm⁻¹. Similar results have only been reported previously for α -halo esters and α -halo ketones (12, pp. 443–509). The shift is shown by α -halo alicyclic ketones only when the halogen is equatorial and approximately coplanar with the carbonyl group. The larger shift of 32 cm⁻¹ shown by the tribromolactone (III*h*) may be compared with the very exceptional shifts shown by esters of perfluoroalkyl carboxylic acids (34).

EXPERIMENTAL

Methyl fluorene-9-carboxylate was prepared and alkylated as described elsewhere (2, 3).

Lactone of 9-(2'-Hydroxyethyl)-fluorene-9-carboxylic acid (IIIa)

Methyl fluorene-9-carboxylate (0.7 g) and 2-bromoethanol gave the lactone, which crystallized from benzene as long white needles (0.5 g), m.p. 184–185°. Found: C, 82.56; H, 5.47%. Calculated for C₁₆H₁₂O₂: C, 82.73; H, 5.21%.

Reduction with ethereal lithium aluminum hydride gave an almost quantitative yield of 9-(2'-hydroxyethyl)-9-fluorenylmethanol, crystallizing from benzene-hexane as small colorless needles, m.p. 94-95°. Found: C, 80.0; H, 6.59%. Calculated for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

Methyl fluorene-9-carboxylate and methyl bromoacetate gave methyl 9-carbomethoxymethylfluorene-9-carboxylate (88%), which formed colorless prisms from methanol, m.p. 91–92°. Found: C, 72.84; H, 5.60%. Calculated for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44%. Reduction with ethereal lithium aluminum hydride gave the diol described above, identity being established by mixed melting point determination and by comparison of infrared spectra.

Lactone of 9-(3'-Hydroxypropyl)-fluorene-9-carboxylic acid (IVa)

Methyl fluorene-9-carboxylate (0.7 g) and pure 3-chloropropanol (b.p. 69.5–70.0° at 19 mm; $n_{\rm D}^{24}$ 1.4487) gave the lactone, which formed colorless, well-defined prisms

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(0.64 g) from benzene-hexane, m.p. 232-234°. Found: C, 81.69; H, 5.62%. Calculated for C₁₇H₁₄O₂: C, 81.58; H, 5.64%.

γ-Lactone of 9-(2',3'-Dihydroxypropyl)-fluorene-9-carboxylic acid (IIIb)

Methyl fluorene-9-carboxylate and pure 2,3-dihydroxypropyl chloride gave the γ -lactone, which crystallized from chloroform-hexane as small colorless prisms (65–78%), m.p. 180–181°. Found: C, 76.85; H, 5.54%. Calculated for C₁₇H₁₄O₃: C, 76.67; H, 5.30%.

The infrared spectrum of a chloroform solution of the material retained in the mother liquors suggested the presence of methyl fluorene-9-carboxylate ($\nu_{C=0}$ 1760 cm⁻¹), further amounts of the γ -lactone (1770 cm⁻¹), and traces of the isomeric δ -lactone (1730 cm⁻¹).

Lactone of 9-(2'-Hydroxy-2'-phenylethyl)-fluorene-9-carboxylic acid (IIIc)

Methyl 9- ω -phenacylfluorene-9-carboxylate (6) (0.8 g) was reduced with a solution of sodium borohydride (0.5 g) in methanol (20 ml). The lactone separated from benzene-hexane as radiating clusters of elongated prisms (0.65 g), m.p. 180–181°, depressed to 165–171° by addition of the starting keto ester (m.p. 184–185°). Found: C, 84.49; H, 5.05%. Calculated for C₂₂H₁₆O₂: C, 84.59; H, 5.16%.

Trans Lactone of 9-(2'-Hydroxycyclohexyl)-fluorene-9-carboxylic acid (VI)

Methyl fluorene-9-carboxylate and cyclohexene oxide gave the lactone, which separated from benzene-hexane as small, well-defined rhombs (88%), m.p. 272–273°. Found: C, 82.74; H, 6.21%. Calculated for $C_{20}H_{18}O_2$: C, 82.73; H, 6.28%.

Alkylation with *cis*-2-chlorocyclohexanol (15) or *trans*-2-bromocyclohexanol (prepared by a general method (35)) gave the same lactone, identified by mixed melting point determinations and by careful comparison of the infrared spectra of chloroform solutions. To obtain good yields of lactone from the bromohydrin it was found necessary to employ 2 moles of methoxide, indicating that the reaction proceeded by prior formation of cyclohexene oxide.

Several attempts to alkylate methyl fluorene-9-carboxylate with *trans*-2-bromocyclopentanol (prepared as for the cyclohexane homologue (35)) were unsuccessful. Occasionally traces of methyl 9-hydroxyfluorene-9-carboxylate were obtained as long white needles from cyclohexane, m.p. 160–161°, identified by comparison with an authentic specimen ((36), m.p. 158–159°).

Halolactones

The 9-alkenylfluorene-9-carboxylic acids were prepared by a general method (3). Methyl esters were characterized only when obtained crystalline. Bromolactones were prepared by adding a slight excess of a solution of bromine in chloroform to the appropriate acid.

9-Allylfluorene-9-carboxylic acid (37), most easily prepared according to reference 2, and the lactone of 9-(3'-bromo-2'-hydroxypropyl)-fluorene-9-carboxylic acid (25) have been described elsewhere. The lactone of 9-(3'-iodo-2'-hydroxypropyl)-fluorene-9-carboxylic acid (24) was more conveniently prepared by Van Tamelen's procedure (17).

The lactone of 9-(3'-chloro-2'-hydroxypropyl)-fluorene-9-carboxylic acid (III*d*), prepared by reaction of the acid with a solution of chlorine in chloroform (9), crystallized as needles from heptane (76%), m.p. 166–167°. Found: C, 71.76; H, 4.65%. Calculated for $C_{17}H_{18}O_2Cl$: C, 71.71; H, 4.60%. The same lactone was obtained in 64% yield from the reaction between thionyl chloride and the hydroxylactone (III*b*), using the conditions described by Berti (9).

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The Lactone of 9-(3'-Bromo-2'-hydroxybutyl)-fluorene-9-carboxylic acid (IIIg)

9-Crotylfluorene-9-carboxylic acid was obtained as small colorless prisms (65%), m.p. 120–122°, after three crystallizations from benzene–hexane. Found: C, 81.99; H, 6.04%. Calculated for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%. Esterification of the pure acid with diazomethane and hydrogenation of the oily methyl ester in methanol over 5% palladized charcoal gave methyl 9-butylfluorene-9-carboxylate, identical with an authentic specimen ((2), m.p. 34.0–34.5°). Saponification gave 9-butylfluorene-9-carboxylic acid, which crystallized as irregular rhombs from benzene, m.p. 115–116°. Found: C, 81.17; H, 6.81%. The identical acid was obtained by saponification of the authentic ester. The alternative product of hydrogenation, methyl 9-s-butylfluorene-9-carboxylate, has m.p. $70-71^{\circ}$ (2).

The bromolactone separated from benzene-hexane as colorless needles (86%), m.p. 149–150°. Found: C, 63.06; H, 4.41%. Calculated for $C_{18}H_{16}O_2Br$: C, 63.00; H, 4.41%. Fractional crystallization of the mother liquors, using infrared spectra as a guide, gave a few milligrams of white needles, m.p. 112–116°, strongly depressed by the above lactone. The infrared spectra suggested that the minor product was the δ -lactone (IVc), originally present in approximately 1–4%.

The Lactone of 9-(2',3',3'-Tribromo-2'-hydroxypropyl)-fluorene-9-carboxylic acid (IIIh)

9-Propargylfluorene-9-carboxylic acid separated from benzene-hexane as colorless needles or prisms (72% based on methyl fluorene-9-carboxylate), m.p. 182–184° with decomposition. Found: C, 82.17; H, 4.85%. Calculated for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%. The methyl ester crystallized as colorless prisms from methanol, m.p. 117–119° (not analyzed). The infrared spectra of solutions of the acid and ester in chloroform showed the characteristic acetylenic C—H stretching band at 3300 cm⁻¹ (8, p. 49).

The tribromolactone formed clusters of prisms (77%) from benzene-hexane, m.p. 155–156° with decomposition and evolution of bromine. Found: C, 42.05; H, 2.56%. Calculated for $C_{17}H_{11}O_2Br_3$: C, 41.92; H, 2.28%.

The Lactone of 9-(2'-Bromo-3'-hydroxy-3'-phenylpropyl)-fluorene-9-carboxylic acid (IVd)

9-Cinnamylfluorene-9-carboxylic acid crystallized from chloroform as well-defined prisms (71%), m.p. 162–163°. Found: C, 84.81; H, 5.72%. Calculated for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%. Hydrogenation in acetic acid over 10% palladium-on-charcoal gave 9-(3'-phenylpropyl)-fluorene-9-carboxylic acid, m.p. 124–126°, identical with an authentic specimen (38).

The crude bromolactone (1 g) was dissolved in cold chloroform (5 ml) and diluted with hot heptane (10 ml); pure lactone separated as small colorless prisms (0.6 g), m.p. 195–197° with decomposition to 9-cinnamylidenefluorene (below). Found: C, 68.24; H, 4.44; Br, 19.94%. Calculated for $C_{23}H_{17}O_2Br$: C, 68.16; H, 4.23; Br, 19.72%. The crude lactone was very unstable but samples of the pure substance have remained unchanged for 2 years.

The lactone (0.1 g) was boiled for 10 minutes with glacial acetic acid (2 ml). When the solution was cooled, 9-cinnamylidenefluorene separated as bright yellow needles (45 mg), m.p. $152-153^{\circ}$ (lit. m.p. $150.5-151.0^{\circ}$ for the all-trans isomer (39)).

The Lactone of 9-(3'-Bromo-2'-hydroxycyclohexyl)-fluorene-9-carboxylic acid (VII)

9-(3'-Cyclohexenyl)-fluorene-9-carboxylic acid, prepared from 3-bromocyclohexene (40), formed large, colorless prisms (73%) from benzene-hexane, m.p. 168–170° with decomposition. Found for a sample dried 12 hours at 80° and 1 mm; C, 82.52; H, 6.35%. Calculated for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

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The bromolactone crystallized from benzene-hexane as colorless needles (89%), m.p. 186-187°. Found: C, 64.92; H, 4.70%. Calculated for C₂₀H₁₇O₂Br: C, 65.05; H, 4.64%.

The Lactone of 9-(3'-Bromo-2'-hydroxycyclopentyl)-fluorene-9-carboxylic acid (VIII)

Methyl 9-(3'-Cyclopentenyl)-fluorene-9-carboxylate

Alkylation of methyl fluorene-9-carboxylate with 3-chlorocyclopentene (41) gave a brown resin. Extraction with boiling heptane and passage of the resulting solution through a short column of activated alumina gave the pure ester, crystallizing from heptane as small colorless needles (67%), m.p. 93-94°. Found: C, 82.56; H, 6.32%. Calculated for C₂₀H₁₈O₂: C, 82.73; H, 6.25%. Hydrogenation in methanol over 5% palladized charcoal gave methyl 9-cyclopentylfluorene-9-carboxylate as elongated prisms from methanol or hexane, m.p. 83.0-84.5°. Found: C, 82.06; H, 6.78%. Calculated for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89%. The same ester was obtained by alkylating fluorene ester with cyclopentyl bromide.

9-(3'-Cyclopentenyl)-fluorene-9-carboxylic acid separated from benzene-hexane as prismatic needles, m.p. 184-186°, after a change of crystalline form at 160-161°. Found: C, 83.12; H, 5.30%. Calculated for C₁₉H₁₆O₂: C, 82.78; H, 5.54%.

The bromolactone formed small prisms (45%) from benzene-hexane, m.p. 208-210°. Found: C, 64.17; H, 4.10%. Calculated for C19H15O2Br: C, 64.24; H, 4.26%.

The Lactone of 5-Bromo-4-hydroxy-2,2-diphenylpentanoic acid (IX)

Allyldiphenylacetic acid was prepared as described (42) for methyldiphenylacetic acid. It formed rosettes of prisms (77%) from benzene-hexane, m.p. 143-144° (lit. m.p. 142-143° (43)). The lactone of 5-bromo-4-hydroxy-2,2-diphenylpentanoic acid (IX) crystallized as large prisms from benzene-hexane, m.p. 88-89° (lit. m.p. 87-88° (22)). Found: C, 62.03; H, 4.39%. Calculated for C₁₇H₁₅O₂Br: C, 61.64; H, 4.57%.

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