158. *The Preparation and Properties of β-9-Fluorenylidenepropionic Acid.*

By D. M. W. Anderson, Neil Campbell, J. T. Craig, and D. A. Crombie.

The constitution of β-9-fluorenylidenepropionic acid (II) has been established and the chemical and spectral properties of the acid and its derivatives are reported.

9-Formylfluorene and malonic acid in piperidine condense to give β-9-fluorenylidenepropionic acid [1] (II), m. p. 202—203°, which is also obtained by the interaction of 9-formylfluorene and ethyl cyanoacetate followed by hydrolysis and decarboxylation of the product (I). This intermediate is colourless in the solid state and in hexane, but gives a yellow solution in ethanol or piperidine, probably owing to the colourless form's having structure (I) which tautomerises [2] to the yellow βγ-unsaturated ester form, $:CH\cdot CH(CN)\cdot CO_2Et$. This is substantiated by the ultraviolet spectrum in hexane which resembles that of fluorene, a similarity which disappears when the solvent is changed to ethanol. Similar colour changes, however, are sometimes observed in fluorene derivatives which cannot tautomerise, the colourless, crystalline 9-diphenylmethylenefluorene, for instance, giving yellow solutions or melts.[3] The position of the double bond in the

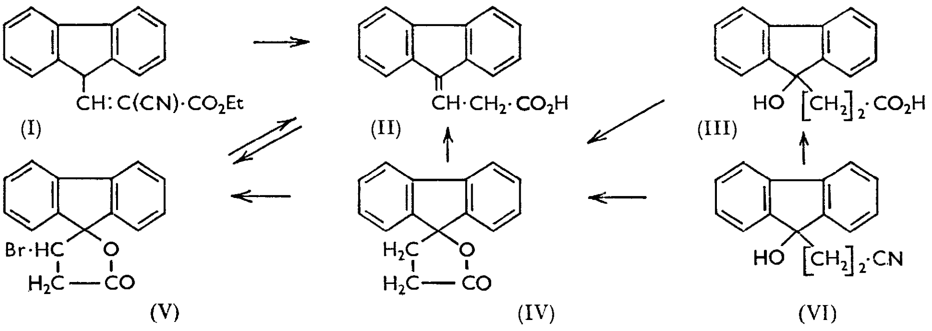
---

[1] Borsche and Niemann, *Ber.*, 1936, **69**, 1998.

[2] Cf. Meyer and Gottlieb-Billroth, *Ber.*, 1921, **54**, 575; Kuhn and Levy, *Ber.*, 1928, **61**, 2240.

[3] Klinger and Lonnes, *Ber.*, 1896, **29**, 2157.

unsaturated acid (II) is suggested by the colourless ureide formed by the acid with di-*p*-dimethylaminophenylcarbodi-imide.[4] These results are in conflict with those of Campbell and Fairfull,[5] who assigned m. p. 137° to the acid (II), which they prepared by the alkaline hydrolysis of β-(9-hydroxy-9-fluorenyl)propionitrile (VI) and subsequent treatment with mineral acid; they gave m. p. 202° for the corresponding lactone (IV). We have therefore re-investigated this hydrolysis and find that some of the data reported by Campbell and Fairfull are erroneous and that depending on the conditions the product may be β-(9-hydroxy-9-fluorenyl)propionic acid (III), m. p. 140°, or the lactone (IV), m. p. 133—134°. The constitution of the lactone (IV) is established by the infrared band at 1772 cm.$^{-1}$ characteristic of five-membered saturated lactones,[6] by the similarity of its ultraviolet spectrum to those of fluorene and particularly 9-ethylfluorene-9-ol[7] (see Table), by the positive test with hydroxylamine,[8] and by ring-opening with sulphuric acid to give β-9-fluorenylidenepropionic acid (II).[9] The lactone with bromine in acetic acid gives the bromo-lactone (V). That the acid (II) is a βγ-unsaturated acid is proved by catalytic hydrogenation or reduction with hydriodic acid and phosphorus to β-9-fluorenylpropionic acid,[10] and by the ultraviolet spectrum (see Table) which lacks the 250—300 mμ band and the less intense band at 300—310 mμ characteristic of fluorene and fluorenyl derivatives[11] (see Table) and exhibits absorption similar to that of fluorenylidene derivatives[11] such as 9-ethylidenefluorene[7,12] and fluorenylideneacetic acid (see Table). It shows infrared absorption at 1718 cm.$^{-1}$ associated rather with a saturated or βγ-unsaturated acid than with an αβ-unsaturated acid (1710—1690 cm.$^{-1}$).[13] We were unable to convert the acid into the lactone (IV), which, however, is easily obtained by dehydration of the hydroxy-acid (III). This failure of a βγ-unsaturated acid to undergo lactonisation is contrary to the lactonisation of many βγ-unsaturated acids[14] and is in contrast to the behaviour of the structurally analogous diphenylvinylacetic acid which in acid media is in equilibrium with the lactone and with sulphuric acid gives a 95% yield of the lactone.[9] Efforts to isomerise the βγ- to the αβ-unsaturated acid by alkali failed, confirming the conclusions of earlier workers that γ-phenylbutenoic acids resist isomerisation[15] to the αβ-form.



The unsaturated acid (II) with bromine in acetic acid yields a dibromide which

---

[4] Campbell and Crombie, *Chem. and Ind.*, 1959, 600.

[5] Campbell and Fairfull, *J.*, 1949, 1239.

[6] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 2nd edn., 1958, p. 186.

[7] Bergmann, Heller, and Weiler-Feilchenfeld, *Bull. Soc. chim. France*, 1959, 634.

[8] Feigl, " Qualitative Analysis by Spot Tests," Elsevier, Amsterdam, 3rd edn., 1947, p. 358.

[9] Johnson, Petersen, and Schneider, *J. Amer. Chem. Soc.*, 1947, **69**, 74.

[10] Campbell and Fairfull, *J.*, 1949, 1102.

[11] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," J. Wiley and Co., Inc., New York, 1951, diagrams 311—315.

[12] Greenhow, McNeil, and White, *J.*, 1952, 986; 1953, 3099.

[13] Ref. 6, p. 162.

[14] Farmer, *Ann. Reports*, 1932, **29**, 108.

[15] Linstead and Williams, *J.*, 1926, 2735.

Ultraviolet spectra [wavelength in mμ (log $\varepsilon_{max.}$ in parentheses), solvent ethanol].

9-Ethylidenefluorene [12]	230(4·61)	246(4·46)	255(4·60)	271(4·13)	280(4·15)	297(4·03)	311(4·00)
Fluorenylideneacetic acid	228(4·60)	250(4·46)	258(4·46)		288(4·12)	302(4·13)	315(4·12)
β-Fluorenylidenepropionic acid	230(4·66)	246(4·59)	257(4·61)		280(4·23)	300(4·1)	314(4·09)
Fluorene			262(4·25)	289(3·8)	300(4·0)		
Fluoren-9-ol	228(4·38)	234(4·29)	271(4·14)	296(3·56)	307(3·35)		
9-Methylfluoren-9-ol [a]			274(4·1)	296(3·71)	303(4·32)		
9-Benzylfluoren-9-ol	228(4·37)	236(4·24)	276(4·07)		307(3·51)		
β-(9-Hydroxyfluorenyl)-propionitrile	228(4·35)	236(4·25)	274(4·12)		307(3·45)		
Lactone (IV)	228(4·38)	235(4·36)	273(4·10)		302(3·34) *		

* Inflexion. [a] Coombs, *J.*, 1958, 3454.

decomposes so rapidly that we were unable to obtain it pure. We are satisfied, however, that the pure dibromo-acid melts considerably lower than the m. p. 166—167° reported.[5] The dibromo-acid when kept yields the bromo-lactone (V), whose ultraviolet spectrum resembles that of the lactone (IV) although it has a strong band at 1795 cm.$^{-1}$, differing from the 1775 cm.$^{-1}$ exhibited by five-membered lactones.[6] The bromo-lactone and the dibromo-acid give rise to the unsaturated acid (II) when boiled for a short time with zinc and acetic acid.

Both the βγ-unsaturated and the hydroxy-acid show carboxyl absorption at 1718 cm.$^{-1}$ typical of dimerised carboxylic acids,[16] while the hydroxy-acid possesses a sharp hydroxyl band [17] at 3460 cm.$^{-1}$ and an ultraviolet spectrum similar to that of the lactone (IV). The ultraviolet spectra of our fluorenol derivatives illustrate the bathochromic influence of the 9-hydroxyl group on the fluorene spectrum (see Table),[18] giving rise to the characteristic band at 307—310 mμ by which fluorenols can be differentiated from their derivatives such as the alkyl ethers or lactones (*e.g.*, IV).

The Reformatsky reaction between fluorenone and ethyl bromoacetate yields an oil which with boiling formic acid gives ethyl 9-fluorenylideneacetate and the acid.[19] Efforts to increase the length of the carbon chain of this acid by the Arndt–Eistert reaction were unsuccessful.

EXPERIMENTAL

Infrared spectra were obtained on Nujol or hexachlorobutadiene mulls by using a Hilger H800 double-beam spectrophotometer, calibrated with reference to the carbonyl frequency of acetone in carbon tetrachloride (1718 cm.$^{-1}$). Ultraviolet absorption spectra were measured for 95% ethanol solutions (unless otherwise stated) with a Unicam S.P. 500 spectrophotometer.

β-9-*Fluorenylidenepropionic Acid.*—Sodium (1·51 g.) in dry ethanol (27 ml.) was added to ethyl cyanoacetate (7·4 ml.), and the suspension poured on 9-formylfluorene (13 g.). The mixture was warmed for 15 min. and sufficient water was added to give a clear solution. Acidification with concentrated hydrochloric acid gave an oil which was extracted with ether. The extract, after repeated washing with water and drying (Na_2SO_4), yielded on evaporation *ethyl α-cyano-*β-9-*fluorenylacrylate* which separated from methanol in needles (11 g.), m. p. 93—94·5° (Found: C, 79·0; H, 5·2; N, 5·0. $C_{19}H_{15}O_2N$ requires C, 78·9; H, 5·2; N, 4·8%), $\lambda_{max.}$ 250 mμ (log ε 4·68) in ethanol, and 228 (log ε 4·28), 258 (log ε 4·40), 288 (log ε 3·84), and 300 mμ (log ε 3·80) in hexane. The ester (2·23 g.) when boiled for 3 hr. with ethanol (180 ml.) and concentrated hydrochloric acid (180 ml.) yielded β-9-fluorenylidenepropionic acid (1·18 g.), m. p. 198—201° (not depressed when admixed with the acid obtained by the condensation of 9-formylfluorene and malonic acid with pyridine as catalyst [1]), and the *ethyl ester* (1·21 g.), m. p. 73—74° (after trituration and crystallisation from ethanol) (Found: C, 81·3; H, 6·3. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%). The ester was hydrolysed to the acid by boiling with methanol and sodium hydroxide in ½ hr. Boiling the acid (0·5 g.) for ½ hr. with 50% aqueous potassium hydroxide gave fluorene (0·3 g.), m. p. and mixed m. p. 115°.

---

[16] Ref. 6, p. 165.

[17] Ref. 6, p. 96.

[18] Coombs, *J.*, 1958, 3454.

[19] Sieglitz and Jassoy, *Ber.*, 1921, **54**, 2133.

Hydrolysis of β-(9-*Fluorenyl*-9-*hydroxy*)*propionitrile*.—In each of three experiments fluorenol (8 g.) and vinyl cyanide (3 ml.) were added to potassium hydroxide (0·53 g.) in methoxyethanol (48 ml.), and the mixture was heated at 50° for 20 min. and then boiled for 30 min. with potassium hydroxide (40 g.) in water (72 ml.) and 2-methoxyethanol (48 ml.). The mixture was poured into water.

(*a*) In one run the solution was acidified with hydrochloric acid, extracted with ether, and evaporated to give β-(9-*fluorenyl*-9-*hydroxy*)*propionic acid lactone* (2 g.), m. p. 133—134°: after crystallisation from benzene–light petroleum (Found: C, 81·15; H, 5·0. $C_{16}H_{12}O_2$ requires C, 81·3; H, 5·1%), $\nu_{max.}$ 1772 cm.$^{-1}$ (cf. Table).

(*b*) In another run 2 g. of crude material yielded β-(9-*hydroxy*-9-*fluorenyl*)*propionic acid*, m. p. 143—144° after crystallisation from benzene–light petroleum (Found: C, 76·8; H, 5·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·55%), $\lambda_{max.}$ 228 (log ε 4·29), 234 (log ε 4·18), 275 (log ε 4·05), 296 (log ε 3·56), and 307 mμ (log ε 3·55).

(*c*) The crude product after acidification with hydrochloric acid was extracted with ether, and the extract shaken with aqueous sodium carbonate. The carbonate layer with acid gave the hydroxy-acid which, crystallised from benzene–light petroleum, had m. p. 143—144°. The hydroxy-acid (0·5 g.) was boiled for 10 min. with dilute sulphuric acid (12 ml.) and poured into water (12 ml.). The mixture was extracted with ether, and the ether layer shaken with sodium carbonate solution. The ether on evaporation gave the lactone (0·3 g.), m. p. and mixed m. p. 131—133°, while acidification of the sodium carbonate solution yielded β-9-fluorenylidenepropionic acid (0·025 g.), m. p. and mixed m. p. 202—204° (from benzene–light petroleum), subliming in prisms. The acid has a blue fluorescence. The lactone (0·5 g.) was boiled for 2½ hr. in dilute sulphuric acid and poured into water (12 ml.); extraction with ether was followed by shaking the ether with sodium carbonate; evaporation of the ether gave unchanged lactone (0·18 g.), m. p. 132—134°, and acidification of the sodium carbonate layer yielded β-9-fluorenylidenepropionic acid (0·25 g.), m. p. 202—204° (from benzene).

Bromination of β-9-*Fluorenylidenepropionic Acid*.—The reaction is capricious. The unsaturated acid in carbon disulphide with bromine yielded the impure dibromo-acid, m. p. 128—134° (lit., 166—167° [5]) (Found: Br, 38·3. $C_{16}H_{12}O_2Br_2$ requires Br, 40·4%), which decomposed in organic solvents to give the bromo-lactone. Bromine (0·2 g.) in acetic acid (3 ml.) was added to the unsaturated acid (0·35 g.) in acetic acid (10 ml.) until the colour persisted and most of the solvent was removed at room temperature in a vacuum. Addition of light petroleum gave the *bromo-lactone* (0·25 g.), compact prisms (from benzene–light petroleum), m. p. 165—166° (Found: C, 60·8; H, 3·6; Br, 25·5. $C_{16}H_{11}BrO_2$ requires C, 61·0; H, 3·5; Br, 25·4%), $\lambda_{max.}$ 228 (log ε 4·49), 235 (log ε 4·44), and 274 mμ (log ε 4·14), $\nu_{max.}$ 1795 cm.$^{-1}$. Frequently the product was a mixture of dibromo-acid and bromo-lactone, each (0·16 g.) of which when heated with zinc dust (0·6 g.) and acetic acid for 4 min. yielded β-9-fluorenylidenepropionic acid. Keeping the lactone (0·3 g.) of β-(9-hydroxy-9-fluorenyl)propionic acid suspended in acetic acid (4 ml.) overnight with bromine (0·2 g.) in acetic acid (2 ml.) and adding water gave impure bromo-lactone, m. p. and mixed m. p. 159—162° (after three crystallisations from benzene–light petroleum).

9-*Fluorenylidenacetic Acid*.—Fluorenone (9 g.) and ethyl bromoacetate (10 g.) in dry benzene (40 ml.) were heated for 2 hr. with zinc wool (3·3 g.) which had been washed with hydrochloric acid, ethanol, and ether, and dried. The oily product, obtained in the usual way, was boiled with 85% formic acid (75 ml.) for 1 hr., and water and formic acid were removed under reduced pressure. The residual red oil when dissolved in boiling methanol and cooled yielded ethyl 9-fluorenylideneacetate, yellow needles (8 g.), m. p. 72° (lit., 77°). The ester (8 g.) was boiled for 1 hr. with 2N-sodium hydroxide (200 ml.) and ethanol (40 ml.). Acidification yielded 9-fluorenylideneacetic acid (5·8 g.), yellow prisms (from aqueous acetic acid), m. p. 225—228° (lit., 227—228°), $\lambda_{max.}$ 228, 250, 258, 288, 302, and 315 mμ (log ε 4·60, 4·46, 4·60, 4·12, 4·13, and 4·12).

Thanks are expressed to the Department of Scientific and Industrial Research for maintenance grants (to J. T. C. and D. A. C.).

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF EDINBURGH. [*Received, August* 10*th*, 1959.]