Thermolysis of Salts of 2-Substituted Acrylic Acids. Novel Reduction of a Vinyl Bromide

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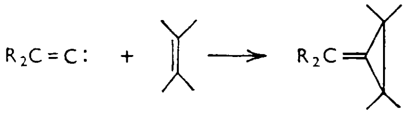
Upon heating the sodium or silver salts of 2-chloroacrylic, 2-bromo-3,3-diphenylacrylic, and α-bromofluorenylideneacetic acid alone, in inert solvents, or in olefins, decarboxylation results and, where possible, rearrangement to acetylenes. Similarly, methyl fluorenylideneacetates are demethylated and decarboxylated on heating with sodium iodide. These decompositions do not involve carbenes.

Treatment of esters of α-bromofluorenylideneacetic acid with alcoholic alkali or alkoxides causes replacement of bromine by hydrogen, to give fluorenylideneacetic acid in high yield, probably by hydride transfer from the alkoxide ion to the electrophilic double bond.

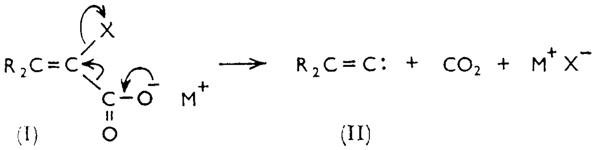
In an investigation of new general synthetic routes to alkylidenecyclopropanes, we considered the generation of alkylidenecarbenes and their addition to olefins (Scheme 1).



Scheme 1

At the start of our work, very few reactions of this type had been reported. Hartzler[1] had added the resonance-stabilised dimethylallenecarbene to olefins, and Curtin[2] had investigated the base-induced α-elimination of hydrogen halide from 2,2-disubstituted 1-halogenoethylenes; the intermediates were not trapped with olefins. During this investigation there have been reports of the generation and trapping of alkylidenecarbenes, mainly involving base-induced eliminations from halogeno-olefins.[3]

Alkylidenecarbenes could, in principle, be generated by loss of metal halide and carbon dioxide from salts of 2-halogenoacrylic acids (I) in a reaction analogous to that in which dichlorocarbene is formed by thermolysis of sodium trichloroacetate. This reaction has the advantage that it does not need a base to generate the carbene, so any alkylidenecarbenes formed might be less likely to rearrange.



The thermal decomposition of sodium 2-chloroacrylate (I; R = H, M = Na, X = Cl) was studied first. The salt decomposed above 150°, the extent of decomposition being measured by precipitation of the liberated chloride as silver chloride. Whether the reaction was performed in the presence of an olefin or not, the only organic product detected was acetylene. Thus, even if acetylene was formed by rearrangement of the carbene (II; R = H) (and other mechanisms are more likely), this must rearrange faster than it adds to olefins. This result was not surprising; however, we considered that if the groups R were much more bulky rearrangement of the intermediate might be slower or possibly inhibited completely. Sodium 2-bromo-3,3-diphenylacrylate (I; R = Ph, M = Na, X = Br) was synthesised by a modification of the literature method.[4] It decomposed above 180° to give diphenylacetylene as the only organic product. Köbrich and Fröhlich[5] have since reported a detailed investigation of this same reaction and have isolated small amounts of products besides diphenylacetylene. Thus the introduction of phenyl groups at the β-position did not prevent rearrangement.

α-Bromofluorenylideneacetic acid (III; R = H) was synthesised since in this case an analogous rearrangement would generate phenanthryne rather than a stable acetylene, so that there seemed less likelihood of rearrangement. The acid, which had not previously been reported, was made by the bromination and dehydrobromination of ethyl fluorenylideneacetate (IV; R = Et) followed by hydrolysis of the unsaturated bromo-ester (III; R = Et). Hydrolysis of the bromo-ester (III; R = Et) was abnormal, however, and only if mild conditions (warm 2% aqueous alcoholic potassium hydroxide) were used, could the bromo-acid (III; R = H) be obtained. If the esters were heated instead with sodium or potassium ethoxide in ethanol, potassium t-butoxide in t-butyl alcohol, or even with concentrated ethanolic potassium hydroxide, the product was predominantly fluorenylideneacetic acid (IV; R = H) (up to 80% yield). The bromo-acid (III; R = H) was similarly converted into the acid (IV; R = H) (80%) by ethanolic potassium ethoxide. However, the acid (III; R = H) was unchanged when heated with potassium t-butoxide in t-butyl alcohol. The corresponding ethyl ester of 2-bromo-3,3-diphenylacrylic acid was hydrolysed quite normally to the bromo-acid under conditions more vigorous than those which effected

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[1] H. D. Hartzler, *J. Amer. Chem. Soc.*, 1959, **81**, 2024.

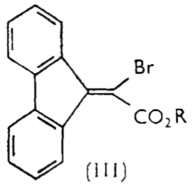
[2] D. Y. Curtin and E. W. Flynn, *J. Amer. Chem. Soc.*, 1959, **81**, 4714; D. Y. Curtin and W. H. Richardson, *ibid.*, 1959, **81**, 4719.

[3] M. Tanabe and R. A. Walsh, *J. Amer. Chem. Soc.*, 1963, **85**, 3522; H. D. Hartzler, *ibid.*, 1964, **86**, 526; K. L. Erickson and J. Wolinsky, *ibid.*, 1965, **87**, 1142; N. Wakabayashi, *J. Org. Chem.*, 1967, **32**, 489.

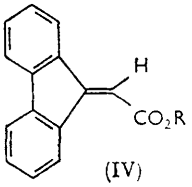
[4] D. D. E. Newman and L. N. Owen, *J. Chem. Soc.*, 1952, 4722.

[5] G. Köbrich and H. Fröhlich, *Angew. Chem. Internat. Edn.*, 1964, **3**, 445.

abnormal reactions of the fluorenylidene esters. Thus the abnormal reaction is likely to be due to the special properties of the fluorenylidene system, particularly the enhanced stability of the fluorenyl anion. A possible addition–elimination mechanism involves hydride exchange between the alkoxide ion and the electrophilic α-carbon atom (Scheme 2), similar to that recently proposed for the reduction of ketones with potassium hydroxide in ethylene glycol.[6] This mechanism accords with the observation that the bromo-acid (III; R = H) is unaffected by potassium t-butoxide in t-butyl alcohol, where there is no source of hydride ions. However, the bromo-ester (III; R = Et) gave an appreciable amount (14%) of fluorenylideneacetic acid, where the only hydride source is the one mol. of ethoxide formed by ester exchange. In no experiment was any replacement of bromine by hydroxy- or ethoxy-groups detected.



(III)



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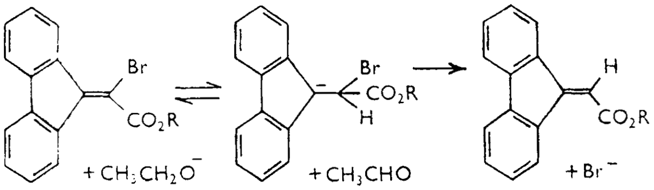
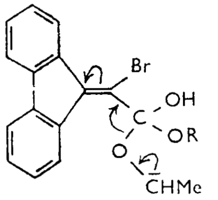


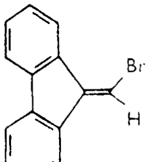
SCHEME 2

We are grateful to a Referee for suggesting an alternative mechanism: attack of the ester carbonyl group by ethoxide ion gives the tetrahedral intermediate which undergoes intramolecular proton transfer to give the carbanion (V); (V) then loses acetaldehyde as shown to give, after ketonisation, the same carbanion as in Scheme 2. This sequence is analogous to that sometimes found in the Wittig rearrangement,[7] though much more reactive hydrogen atoms and vigorous conditions seem to be required for this.



(V)

The sodium salt of the acid (III; R = H) was decomposed in dimethyl sulphoxide or diethylene glycol diethyl ether at temperatures between 160° and 190°. Two products were isolated and identified as 9-bromomethylenefluorene (VI) and 1,2-difluorenylidene-ethane (VII), by comparison with their known properties. The dimeric product (VII) was probably formed from the decarboxylation product (VI), since (VI) was found to be convertible into (VII) under these conditions.



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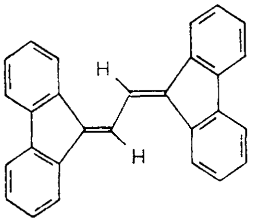
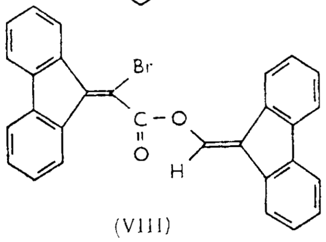


(VII)



(VIII)

The silver salt of acid (III; R = H) was also made and decomposed under similar conditions. Besides the above two compounds, there was a third minor product which was assigned the ester structure (VIII) from analytical and spectral data. It was presumably formed by a reaction of the bromo-olefin (VI) and the silver salt analogous to the hydride reduction described above.

A third method of decomposition in which the methyl ester (III; R = Me) was heated in dimethyl sulphoxide with sodium iodide (conditions under which the ester should be demethylated and the carboxylate anion produced) gave the decarboxylated compound (VI) as the sole product in 94% yield. Thus, although the anion decarboxylated readily, it did not lose bromine. This suggests that the rearrangements observed in the other decompositions of substituted acrylate salts were rearrangements of the carbanion, not the carbene, the halide ion being lost during rearrangement.

In order to achieve a 1,1-elimination, the α-substituent has therefore to be a better leaving group than bromine. The *p*-bromobenzenesulphonate group was chosen, and the ester (IX; R = CO_2Me) was synthesised from methyl fluorene-9-glyoxylate,[8] which is shown by its infrared spectrum to be completely enolised in the solid state. The ester (IX; R = CO_2Me) with sodium iodide in dimethylformamide was demethylated and decarboxylated to give (IX; R = H) in a reaction entirely analogous to the formation of (VI) above.

In refluxing diethyleneglycol diethyl ether (190°) a completely different, and more complex reaction occurred. There were two major products, and several minor ones, but since all of these contained sulphur they

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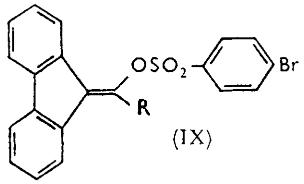
[6] D. C. Kleinfelter, *J. Org. Chem.*, 1967, **32**, 840.

[7] H. E. Zimmerman, 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, London, 1963, Part I, p. 372.

[8] A. Campbell and S. H. Tucker, *J. Chem. Soc.*, 1949, 2623.

were very unlikely to have been formed *via* fluorenylidene carbene intermediates. The identification of these products and their unusual mode of formation will be reported separately.

Hartzler[9] reported an investigation of the decomposition of silver salts of acids (I; R = Me and Ph, X = Br) and (III; R = H) while this work was in progress. There was no evidence of the formation of carbenes. Curtin and his co-workers[10] have since reported the generation and trapping of fluorenylidene carbene by the reaction of 9-aminomethylenefluorene with isopentyl nitrite.



(IX)

EXPERIMENTAL

Sodium 2-chloroacrylate (71%) was precipitated when an equimolecular amount of sodium hydroxide in aqueous ethanol was added to an ethanolic solution of the acid. 2-Bromo-3,3-diphenylacrylic acid was prepared by the addition of bromine to ethyl 3,3-diphenylacrylate and hydrolysis and dehydrobromination of the dibromo-ester.[4] The yield of final product is improved if these last two steps are performed separately. The dibromo-ester loses hydrogen bromide very readily, on heating or on treatment with tertiary amines. In one preparation, the addition of bromine in chloroform to ethyl 3,3-diphenylacrylate gave *ethyl 2-bromo-3,3-diphenylacrylate* directly, m. p. 66° (Found: C, 61·7; H, 4·6. $C_{17}H_{15}BrO_2$ requires C, 61·7; H, 4·5%), $\nu_{max.}$ 1716 cm.$^{-1}$. This heated with 5% aqueous ethanolic potassium hydroxide for 15 min. at 100° and the solution was diluted with water, cooled, and acidified, to give 2-bromo-3,3-diphenylacrylic acid (95%), m. p. to 149—150° (from cyclohexone) (lit.,[4] m. p. 150°). The sodium salt was made by addition of the calculated weight of sodium hydroxide in ethanol to an ethanolic solution of the acid and drying the precipitate.

α-Bromofluorenylideneacetic Acid (III; R = H).—Ethyl fluorenylideneacetate (IV; R = Et), m. p. 77°, was prepared from fluorenone and ethyl bromoacetate.[11] Fluorenylideneacetic acid, obtained by hydrolysis of the ester, had m. p. 220—224° (decomp.) (from ether–cyclohexane) (lit.,[11] m. p. 227—228°) (Found: C, 81·1; H, 4·5. Calc. for $C_{15}H_{10}O_2$: C, 81·1; H, 4·5%). To the ester (IV; R = Et) (20 g.) in dry carbon tetrachloride (80 ml.), bromine (13 g.) in carbon tetrachloride (20 ml.) was added. The solution was evaporated after 1 hr. to give *ethyl α-bromo-α-(9-bromofluorenyl)acetate* (30 g.), 91%) as a pale yellow solid, m. p. 107° (from ethanol) (Found: C, 50·3; H, 3·5. $C_{17}H_{14}Br_2O_2$ requires C, 49·8; H, 3·4%), $\nu_{max.}$ 1745 cm.$^{-1}$.

The dibromo-ester (20 g.) was heated under reflux with triethylamine (10 ml.) in benzene (100 ml.) for 10 min. to give *ethyl α-bromofluorenylideneacetate* (III; R = Et) (13 g., 80%), m. p. 91° (from ethanol and from cyclohexane) (Found: C, 62·0; H, 3·9; Br, 24·0. $C_{17}H_{13}BrO_2$ requires C, 62·0; H, 3·9; Br, 24·3%). *Methyl α-bromofluorenylideneacetate* (III; R = Me), m. p. 93·5° (Found: C, 60·7; H, 3·5. $C_{16}H_{11}BrO_2$ requires C, 60·95; H, 3·6%) was prepared similarly. The ethyl ester was hydrolysed by heating it with 2% aqueous alcoholic potassium hydroxide for 30 min. on a steam-bath to give *α-bromofluorenylideneacetic acid* (90%), m. p. 178° (from benzene) (Found: C, 59·7; H, 2·8. $C_{15}H_9BrO_2$ requires C, 59·8; H, 3·0%) $\nu_{max.}$ 1686, 1621, 1597, 1399, 1299, 1261, 1038, 1002, 933, 857, 775, 756, and 725 cm.$^{-1}$. The sodium salt was prepared by adding an equimolar amount of sodium hydroxide to an ethanolic solution of the acid and evaporating the solution to dryness. The *silver salt* was prepared by adding an excess of alcoholic silver nitrate to an ethanolic solution of the acid. It crystallised slowly as pale yellow needles which contained ethanol of crystallisation (Found: C, 44·3; H, 3·0. $C_{15}H_8AgBrO_2$, C_2H_5OH requires C, 44·9; H, 3·1%).

Reductive Hydrolysis of Ethyl α-Bromofluorenylideneacetate (III; R = Et) *and Reduction of α-Bromofluorenylideneacetic Acid* (III; R = H).—(i) The ester (III; R = Et) (0·5 g.) was added to a hot solution of potassium hydroxide (2 g.) in water (1 ml.) and ethanol (20 ml.). After 1 hr. at 100° the solution was diluted with water, cooled, and acidified to give a gum, which was a mixture of the bromo-acid (III; R = H) and the fluorenylideneacetic acid (IV; R = H) (t.l.c.).

(ii) With sodium (0·5 g.) in ethanol (10 ml.) under the same conditions, the ester (III; R = Et) gave only the fluorenylideneacetic acid (90%) (i.r.), m. p. 210—215° (decomp.).

(iii) The ester (III; R = Et) (1·0 g.) was added to potassium t-butoxide solution [potassium (1·6 g.) in dry t-butyl alcohol (30 ml.)] and the solution was heated under reflux for 0·5 hr. The dark solution was diluted with water (13 ml.) and heated under reflux for 4 hr. More water (20 ml.) was added, the butanol was removed on a rotary evaporator, and the reaction mixture was washed with ether. The aqueous layer was acidified with conc. hydrochloric acid and extracted with ether to give a gum (200 mg.) which on trituration with a little ether gave fluorenylideneacetic acid (IV; R = H) (i.r.), m. p. 209—215° (decomp.) (93 mg., 14%).

(iv) When the bromo-acid (III; R = H) was treated exactly as in (iii) it was recovered unchanged (95%), m. p. 172—175°. No other acid products could be detected.

(v) With potassium ethoxide (3·0 g. potassium in 30 ml. ethanol) under the same conditions, the bromo-acid (III; R = H) (0·50 g.) gave the fluorenylidene acid (IV; R = H) (95%), m. p. 209—214° (decomp.), as the only acidic product.

Hydrolysis of Ethyl 2-Bromo-3,3-diphenylacrylate.—The ester (0·10 g.) was heated under reflux with ethanolic potassium ethoxide [potassium (0·5 g.) in ethanol (5 ml.)] for 2 hr., water (5 ml.) was added, and the ethanol was removed on the rotary evaporator; the solution was cooled, diluted with water (15 ml.), washed with ether, acidified with conc. hydrochloric acid, and extracted with ether to give 2-bromo-3,3-diphenylacrylic acid (i.r.), m. p. 147—148° (87%) (from cyclohexane).

Methyl α-(p-Bromobenzenesulphonyloxy)fluorenylideneacetate (IX; R = CO_2Me).—Methyl fluorene-9-glyoxylate,

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[9] H. D. Hartzler, *J. Org. Chem.*, 1964, **29**, 3414.

[10] D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Amer. Chem. Soc.*, 1965, **87**, 863.

[11] A. Sieglitz and H. Jassoy, *Ber.*, 1921, **54**, 2133.

prepared (59%) by the method of Campbell and Tucker[8] from fluorene and dimethyl oxalate, had m. p. 120—130° depending on the rate of heating (lit.,[8] m. p. 115—120°) (Found: C, 75·5; H, 4·9. Calc. for $C_{16}H_{12}O_3$: C, 76·2; H, 4·8%) $\nu_{max.}$ 3425, 1718 cm.$^{-1}$. This ester (10 g.) in dry methanol (30 ml.) was added to sodium methoxide [sodium (0·9 g.) in methanol (30 ml.)] at 0°. *p*-Bromobenzenesulphonyl chloride (9 g.) in methanol (40 ml.) was added and the mixture was stirred for 24 hr. The precipitate was collected, washed with dilute aqueous sodium hydroxide and with water, and dried, to give the *ester* (IX; R = CO_2Me) (14 g., 71%), m. p. 123° (from methanol–acetone) (Found: C, 56·3; H, 3·2. $C_{22}H_{15}BrO_5S$ requires C, 56·05; H, 3·2%), $\nu_{max.}$ 1736 cm.$^{-1}$; $\lambda_{max.}$ 207 (ε 36,100), 225 (37,600), 254 (39,900), 262 (48,700), and 318 mμ (15,400). The m-*nitrobenzenesulphonyl derivative* was prepared similarly, m. p. 146° (from methanol–acetone) (Found: C, 60·15; H, 3·7. $C_{22}H_{15}NO_7S$ requires C, 60·45; H, 3·4%).

Thermolysis of Sodium 2-Chloroacrylate.—(i) Sodium 2-chloroacrylate (5 g.) and diethyl fumarate (10 ml.) were stirred and heated at 150° for 5 hr. The mixture was cooled, diluted with ether, and filtered. The precipitate was dissolved in nitric acid (50%; 4 ml.) and an excess of aqueous silver nitrate was added to give silver chloride (3%).

(ii) The experiment was repeated with heating at 180° for 8 hr. to give silver chloride (23%). The liquid portion of the reaction mixture was uncontaminated diethyl fumarate [g.l.c., Pye Argon chromatograph with a polyethylene glycol adipate (10% on Celite) column at 150°]. The experiment was repeated with heating at 180° for 40 hr. and the liquid portion of the reaction mixture was again uncontaminated diethyl fumarate (g.l.c., as above).

(iii) Sodium 2-chloroacrylate (5 g.) was heated under reflux with dec-1-ene (15 ml., b. p. 169°) for 48 hr. The liquid portion of the reaction mixture was uncontaminated dec-1-ene (g.l.c., as above).

(iv). Solid sodium 2-chloroacrylate was gently heated until decomposition began. Acetylene was evolved as shown by the decolourisation of aqueous potassium permanganate and the formation of a red-brown precipitate with ammoniacal cuprous chloride solution.

Thermolysis of Sodium 2-Bromo-3,3-diphenylacrylate.—(i) Sodium 2-bromo-3,3-diphenylacrylate (0·5 g.) was heated in a Wood's metal bath and began to decompose at 180°. The bath was heated to 250° and maintained at this temperature for 20 min. The mixture was cooled and extracted with ether to give diphenylacetylene (i.r.) (39%), m. p. 55—58° and mixed m. p. 56—59°.

(ii) Sodium 2-bromo-3,3-diphenylacrylate (2·0 g.) was heated under reflux in diethyl fumarate (15 ml.) for 2 hr. The mixture was cooled, filtered, and the solution was evaporated by under reduced pressure to leave a semisolid mass which crystallised from light petroleum to give diphenylacetylene (24%), m. p. and mixed m. p. 56—59°.

Thermolysis of Sodium α-Bromofluorenylideneacetate.—The salt (2 g.) in diethyleneglycol diethyl ether (25 ml.) was heated for 4 hr. at 190°. On cooling the solution, orange crystals of 1,2-difluorenylidene-ethane (VII) (30 mg.) separated, and were purified by sublimation at 220°/0·1 mm.; the crystals sublime at 360° (lit.,[12] m. p. 355°) (Found: C, 94·55; H, 5·1. Calc. for $C_{28}H_{18}$: C, 94·9; H, 5·1%) $\lambda_{max.}$ 240 (ε 47,200), 268 (40,500), 277 (34,200), 409 (31,500), 435 mμ (29,200), corresponding to the u.v. spectrum reported.[12] The original filtrate was evaporated, the residue was extracted with water and the aqueous extract was acidified with nitric acid; an excess of silver nitrate was added to precipitate silver bromide (58%). The remainder of the reaction mixture was dissolved in benzene and chromatographed on alumina to give 9-bromomethylenefluorene (VI) (30 mg.), m. p. 69—70° (lit.,[13] m. p. 72·5—73°) as the only crystalline substance. The other fractions were bromine-containing gums which could not be characterised.

Thermolysis of Silver α-Bromofluorenylideneacetate.—The silver salt (0·8 g.) was heated to 160° in dimethyl sulphoxide (10 ml.) under nitrogen. There was a rapid evolution of gas, and the solution became dark green and cloudy. After 30 min. it was cooled, poured into water (50 ml.), extracted with ether, and the extract was washed with water, dried, and evaporated to 5 ml.

α-*Fluorenylidene α-bromofluorenylideneacetate* (VIII) (60 mg.) separated as yellow crystals, m. p. 172° (Found: C, 73·4; H, 3·6%; *M*, 477. $C_{29}H_{17}BrO_2$ requires C, 73·0; H, 3·6%; *M*, 477), $\nu_{max.}$ 1730 cm.$^{-1}$; $\lambda_{max.}$ (in Et_2O) 251 (ε 52,300), 260 (79,400), and 322 mμ (22,400). After removing this compound, the filtrate was shown (t.l.c.) to contain bromomethylenefluorene (VI) and a trace of the difluorenylidene-ethane (VII); chromatography on alumina gave (VI) (100 mg.).

Bromomethylenefluorene (VI) (20 mg.) was heated at 180° for 30 min. and gave 1,2-difluorenylidene-ethane (VII) (6 mg., 43%) (i.r.) and unchanged bromoethylenefluorene (7 mg., 35%).

Methyl α-Bromofluorenylideneacetate (III; R = Me) *and Sodium iodide.*—The ester (1·0 g.), sodium iodide (2·0 g.), and dimethyl sulphoxide (10 ml.) were heated to 170° under nitrogen. There was a steady evolution of gas. After 40 min. the dark green reaction mixture was cooled and worked up as above. The crude reaction product (0·62 g.) gave bromomethylenefluorene (VI) (0·53 g., 65%) and difluorenylidene-ethane (VII) (5 mg.).

The experiment was repeated but with hydroquinone (10 mg.) present to suppress any radical reactions. The only product isolated was compound (VI) (i.r.) (0·77 g., 94%).

*Methyl α-(*p*-Bromobenzenesulphonyloxy)fluorenylideneacetate* (IX; R = CO_2Me) *and Sodium Iodide.*—The ester (3·0 g.), dry dimethylformamide (25 ml.), and anhydrous sodium iodide (2·5 g.) were heated under reflux for 1 hr., cooled, and poured into water (150 ml.) and extracted with ether to give (p-*bromobenzenesulphonyloxy*)*methylenefluorene* (IX; R = H) (1·0 g., 38%), m. p. 135° (from ether–light petroleum) (Found: C, 58·7; H, 3·2. $C_{20}H_{13}BrO_3S$ requires C, 58·1; H, 3·15%), $\lambda_{max.}$ 205 (ε 27,700), 228 (40,000), 247 (35,300), 256 (43,800), 271 (14,300), and 312 mμ (11,200).

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[12] D. Lavie and E. D. Bergmann, *J. Org. Chem.*, 1953, **18**, 367.

[13] D. F. De Tar, E. Broderick, G. Foster, and B. D. Hilton, *J. Amer. Chem. Soc.*, 1950, **72**, 2183.