**696.** *The Acid-catalysed Self-condensation of* 9-*Methylfluoren*-9-*ol:*
9-*Azido*-9-*methylfluorene and Related Compounds.*

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The compound of empirical formula $C_{28}H_{21}N$ formed in the reaction of
9-methylfluoren-9-ol with hydrazoic and sulphuric acid [1] has been shown by
synthesis to be (9-methyl-9-fluorenyl)-9-phenanthridinylmethane. This and
related reactions, and their mechanisms, are discussed.

WITH hydrazoic and sulphuric acid 9-methylfluoren-9-ol gives 9-methylphenanthridine
(47%) and a neutral substance $C_{28}H_{21}N$ (about 25%),[1] whereas 9-ethyl-, 9-*iso*propyl-, and
9-*tert.*-butyl-fluoren-9-ol [2] give the 9-alkylphenanthridines in yields of over 80% if the
9-azido-9-*tert.*-butylfluorene isolated from the last reaction is included. Also fluoren-9-ol
itself is converted into phenanthridine in high yield.[3] This anomalous behaviour of the
9-methyl derivative has now been further investigated.

The compound $C_{28}H_{21}N$, m. p. 157°, is insoluble in dilute mineral acids, but forms a
1 : 1 picrate. Its ultraviolet absorption spectrum ($\lambda_{max.}$ 255 mμ, log ε 4·69) is very similar
to the algebraic sum ($\lambda_{max.}$ 254 mμ, log ε 4·51) of the spectra of 9-methylfluorene and 9-
methylphenanthridine in the 240—280 mμ region; the compound was shown to be
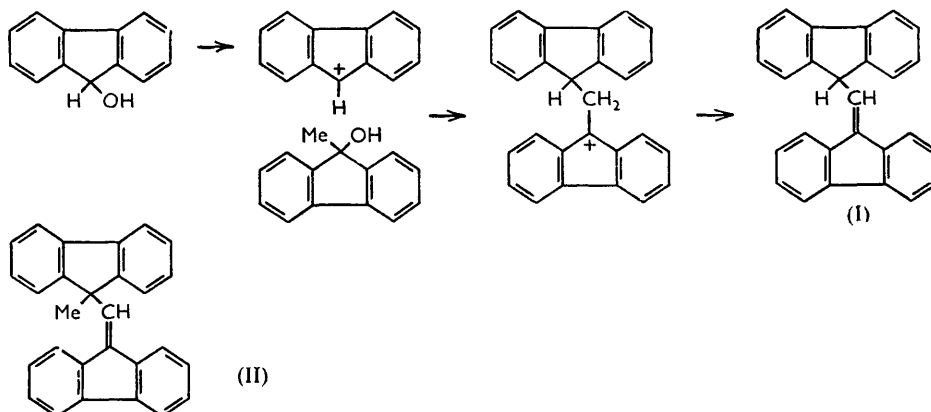
(9-methyl-9-fluorenyl)-9-phenanthridinylmethane (VI) by synthesis from 9-chloromethyl-
phenanthridine and 9-methyl-9-sodiofluorene. It is not formed from 9-methylfluoren-9-ol
by reaction with pre-formed 9-methylphenanthridine in chloroform containing sulphuric
or trichloroacetic acid.

[1] Arcus and Coombs, *J.*, 1954, 4319.
[2] Arcus and Lucken, *J.*, 1955, 1634.
[3] Arcus and Mesley, *J.*, 1953, 178.

Wawzonek and Dufek have shown [4] that fluoren-9-ol, when boiled in acetic acid with 9-methylfluoren-9-ol and hydrochloric acid, gives 9-fluorenyl-9-fluorenylidenemethane (I), probably by electrophilic attack by the 9-fluorenyl cation on 9-methylfluoren-9-ol as in acid-catalysed dimerisation of 1 : 1-diphenylethylene.[5] Treating 9-methylfluoren-9-ol alone with acids under various conditions, in the hope of obtaining the 9-methyl homologue (II), gave only a solid of indefinite melting point. It seems nevertheless that self-condensation does occur. Although 9-azido-9-methylfluorene, m. p. 48°, was obtained in high yield when the fluorenol was added gradually to a solution of trichloroacetic and hydrazoic acid in chloroform,[6] a non-basic compound $C_{28}H_{21}N_3$, m. p. 140° (30% yield), was also isolated when the addition was made rapidly. The ultraviolet absorption spectrum of the latter exhibits the bathochromic shift expected for the introduction of a polar azido-group, and a strong infrared band at 2130 cm.$^{-1}$ is characteristic of azides; [7] 9-azido-9-methyl-fluorene shows a similar band at 2108 cm.$^{-1}$. The structure (9-azido-9-fluorenyl)-(9-methyl-9-fluorenyl)methane (V) is confirmed by synthesis. The condensation between two molecules of 9-methylfluoren-9-ol is presumably followed by reaction of the dimeric cation (III) with hydrazoic acid.

In order to test this reaction sequence (9-hydroxy-9-fluorenyl)-(9-methyl-9-fluorenyl)-methane (VII) was synthesised and its reactions with hydrazoic acid in the presence of (*a*) trichloroacetic and (*b*) sulphuric acid were studied, in the expectation that this alcohol
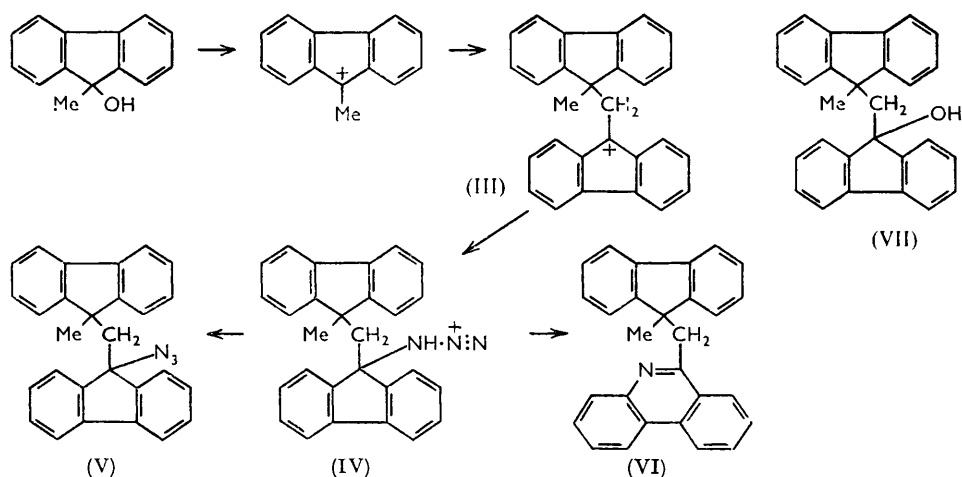
would ionise to yield the cation (III). 9-Methyl-9-sodiofluorene with methylene dibromide gave 9-bromomethyl-9-sodiofluorene, and from the product of the addition of fluorenone to the derived Grignard reagent was isolated the alcohol (VII), m. p. 203—204°. Its ultraviolet absorption spectrum (cf. Table) showed the expected bathochromic shift and marked lessening of the intensities of the two bands in the 290—300 mμ region, characteristic of fluorenols.[8] The yield of alcohol was very poor (7%); a second substance of m. p. 195°, isolated from the reaction mixture in 11% yield, was an unreactive hydro-carbon $C_{30}H_{26}$, whose ultraviolet absorption spectrum was similar to that of 9 : 9-dimethyl-fluorene: [9] it is therefore probably 1 : 2-di-(9-methyl-9-fluorenyl)ethane formed by elimin-ation of magnesium bromide between one molecule of Grignard reagent and one molecule

[4] Wawzonek and Dufek, *J. Amer. Chem. Soc.*, 1956, **78**, 3530.
[5] Evans, Jones, and Thomas, *J.*, 1955, 1824; 1956, 2756.
[6] Arcus, Coombs, and Marks, *J.*, 1957, 4064.
[7] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1954, p. 230.
[8] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," Chapman and Hall, Ltd., London, 1951.
[9] Greenhow and McNeil, *J.*, 1956, 3208.

of bromomethyl derivative. Treatment of (9-hydroxy-9-fluorenyl)-(9-methyl-9-fluorenyl)-methane (VII) with a chloroform solution of hydrazoic and trichloroacetic acid gave an almost theoretical yield of the azide (V), identical with that isolated as described above.

Absorption spectra [$\lambda_{max.}$ (mμ) and log ε].

(9-Methyl-9-fluorenyl)-9-phenanthridinylmethane	$\lambda_{max.}$	—	255	275	290	305
	log ε	—	4·69	4·27 *	4·00 *	3·95
9-Methylfluorene	$\lambda_{max.}$	—	263	—	290	300
	log ε	—	4·40	—	3·61	3·89
9-Methylphenanthridine	$\lambda_{max.}$	—	249	274	285	—
	log ε	—	4·33	3·68 *	3·43 *	—
(9-Azido-9-fluorenyl)-(9-methyl-9-fluorenyl)methane	$\lambda_{max.}$	—	269	—	287	305
	log ε	—	4·31	—	3·84 *	3·70
(9-Hydroxy-9-fluorenyl)-(9-methyl-9-fluorenyl)-methane	$\lambda_{max.}$	—	269	—	294	305
	log ε	—	4·38	—	3·98 *	3·85
9-Methylfluoren-9-ol	$\lambda_{max.}$	—	274	—	296	303
	log ε	—	4·10	—	3·71	4·32
1 : 2-Di-(9-methyl-9-fluorenyl)ethane	$\lambda_{max.}$	230	263·5	—	291·5	303
	log ε	4·19	4·50	—	4·10	4·32
9 : 9-Dimethylfluorene [9]	$\lambda_{max.}$	228	264	—	296	301·5
	log ε	3·85	4·25	—	3·84	4·05

* Inflection.

The alcohol (VII) with hydrazoic and sulphuric acid gave (9-methyl-9-fluorenyl)-9-phenanthridinylmethane (VI) in 50% yield. It is considered that these results strongly support the mechanism proposed above for the formation of these compounds from 9-methyl-fluoren-9-ol.

The product normally to be expected [1] from the acid-catalysed rearrangement of 9-azido-9-methylfluorene is 9-methylphenanthridine. However, in addition, about 10% of compound (VI) was isolated, indicating that addition of hydrazoic acid to the 9-methyl-fluorenyl cation is reversible and that the carbonium ion formed by dissociation of the protonated azide alkylates further azide, which subsequently rearranges. The same conclusion is reached also by consideration of the formation of products (V) and (VI) from 9-methylfluoren-9-ol. Since 9-azido-9-methylfluorene is the sole product when the fluorenol is added slowly to an excess of hydrazoic and trichloroacetic acid, the 9-methylfluorenyl cation reacts faster with hydrazoic acid than with 9-methylfluoren-9-ol; the dimeric cation (III) (giving rise to the dimeric azide) appears only when the 9-methyl-fluorenyl cation is in excess. In the reaction of 9-methylfluoren-9-ol with hydrazoic and sulphuric acid the alcohol is added slowly to an excess of hydrazoic acid, but here, owing to the presence of sulphuric acid, deprotonation of the protonated azide does not occur. Instead, the reversible nature of the cation–hydrazoic acid reaction provides a small concentration of the 9-methylfluorenyl cation for alkylation leading, *via* (III) and (IV), to (9-methyl-9-fluorenyl)-9-phenanthridinylmethane.

Finally, it was found that treatment of (9-azido-9-fluorenyl)-(9-methyl-9-fluorenyl)-methane (V) with sulphuric acid did not yield (9-methyl-9-fluorenyl)-9-phenanthridinyl-methane (VI), but products were formed which were not identified but were presumed to be polymeric. There is thus a substantial difference between the course of reaction when (*a*) the protonated azide (IV) is present at relatively low concentration as a reaction inter-mediate and (*b*) a relatively large concentration of azide (V) is present in equilibrium with its proton-adduct. As deduced in the last section, presumably an equilibrium is set up between the protonated azide (IV) and the corresponding carbonium ion (III), and the latter then attacks unprotonated azide, leading to products containing more than two fluorenyl residues.

Thus the alkylating action of the carbonium ions derived, under appropriate conditions, from both fluorenols and azidofluorenes, leading to substances of molecular size greater than expected, furnishes a consistant account of the products obtained from the above reactions.

EXPERIMENTAL

98% Sulphuric acid was used throughout.

(9-*Methyl*-9-*fluorenyl*)-9-*phenanthridinylmethane*.—To 9-methyl-9-sodiofluorene (from 1·8 g. of 9-methylfluorene [10]) was added a solution of 9-chloromethylphenanthridine [11] (2·2 g.; m. p. 132°) in dry benzene (25 ml.); the mixture was stirred and heated under reflux for 6 hr. Next day, addition of water to the dark mixture gave an orange benzene solution, which was separated, washed with water, and dried (Na$_2$SO$_4$). The oil (3·6 g.) obtained on evaporation mostly dissolved in boiling ethanol (150 ml.) from which were obtained, by successive concentrations, three crops, (i) (0·19 g.), m. p. 225—240°, (ii) (1·10 g.), m. p. 144—148°, (iii) (0·37 g.), m. p. 140—144°. The last two crops were together recrystallised from ethanol four times, yielding needles (0·47 g.), m. p. 157° alone and when mixed with authentic (9-methyl-9-fluorenyl)-9-phenanthridinylmethane.[1]

9-*Bromomethyl*-9-*methylfluorene*.—Methylene dibromide (5·5 ml.) in light petroleum (b. p. 40—60°; 30 ml.) was added to 9-methyl-9-sodiofluorene (from 14·0 g. of 9-methylfluorene), and the mixture was stirred and heated under reflux for 7 hr. under dry nitrogen. Next day the sodium bromide was washed with benzene, and the combined filtrate and washings were evaporated. The residual brown oil was distilled at 138—140°/0·2 mm. (9·5 g.) and crystallised. Recrystallisation from ethanol (25 ml.) gave prisms (6·4 g.) of 9-*bromomethyl*-9-*methylfluorene*, m. p. 59—60° (Found: C, 66·2; H, 4·85; Br, 28·9. C$_{15}$H$_{13}$Br requires C, 65·95; H, 4·65; Br, 29·3%).

(9-*Hydroxy*-9-*fluorenyl*)-(9-*methyl*-9-*fluorenyl*)*methane*.—9-Bromomethyl-9-methylfluorene (2·75 g.) and magnesium turnings (0·25 g.) in dry ether (150 ml.) were boiled under reflux for 10 hr. and left overnight. To the Grignard solution (which still contained a little unchanged magnesium) was added dropwise, with stirring, a solution of fluorenone (1·80 g.) in dry ether (50 ml.). After being heated under reflux for 4 hr., the mixture was decomposed with ice and ammonium chloride. The organic layer afforded a yellow oil (3·8 g.) which, crystallised twice from ethanol, formed prisms (0·4 g.), m. p. 194—195°, of 1 : 2-*di*-(9-*methyl*-9-*fluorenyl*)*ethane* (Found: C, 93·3; H, 6·6. C$_{30}$H$_{26}$ requires C, 93·25; H, 6·75%). This compound was insoluble in, and imparted no colour to, concentrated sulphuric acid.

Evaporation of the original ethanolic filtrate gave a second substance (1·18 g. from 2 batches), melting between 160° and 200°, which on recrystallisation from carbon tetrachloride (75 ml.) yielded small prisms (0·49 g.), m. p. 203—204°, of (9-*hydroxy*-9-*fluorenyl*)-(9-*methyl*-9-*fluorenyl*)-*methane* (Found: C, 90·35; H, 6·1. C$_{28}$H$_{22}$O requires C, 89·9; H, 5·9%).

This alcohol (375 mg.) was added gradually during 20 min. at 25° to a stirred mixture of sodium azide (100 mg.), sulphuric acid (0·40 ml.), and chloroform (2·0 ml.); the sulphuric acid layer became deep red. After a further 20 min. at 25° water (20 ml.) was added giving a green oil and a yellow chloroform solution. The latter was separated, combined with further chloroform extracts, washed with water, and dried (Na$_2$SO$_4$); evaporation left a brown resin (275 mg.) which, from ethanol, gave crops (i) (70 mg.) m. p. 154—155°, and (ii) (120 mg.) m. p. 150—152°, the former melting at 155—157° when mixed with authentic (9-methyl-9-fluorenyl)-9-phenanthridinylmethane.

9-*Azido*-9-*methylfluorene*.—A mixture of trichloroacetic acid (40 g.), chloroform (50 ml.), and sodium azide (4·0 g.) was stirred at 20° for 15 min., and the temperature was then raised to 30°. 9-Methylfluoren-9-ol (6·0 g.), in chloroform (70 ml.), was added during 40 min. and stirring was continued for 2 hr. longer. Water was added, and the chloroform solution was washed free from acid with water, dried (Na$_2$SO$_4$), and evaporated at 40° *in vacuo*, giving a yellow oil which was dissolved in light petroleum (b. p. 40—60°; 10 ml.). There separated columns (5·35 g.) of 9-*azido*-9-*methylfluorene*, m. p. 48—49° (Found: C, 75·05; H, 4·85; N, 18·55. C$_{14}$H$_{11}$N$_3$ requires C, 76·0; H, 5·0; N, 19·0%).

A solution of this azide (1·0 g.) in chloroform (5 ml.) was added dropwise to stirred sulphuric acid (2 ml.) and chloroform (10 ml.) during 30 min. at 20°. The red colour which appeared at each fresh addition of azide rapidly became green. The non-basic, chloroform-insoluble solid which separated when the mixture was poured into water was collected; it (295 mg.) was infusible and insoluble in the usual organic solvents. Evaporation of the chloroform solution and recrystallisation of the residue from ethanol gave (9-methyl-9-fluorenyl)-9-phenanthridinyl-methane (100 mg.), m. p. 150° (mixed m. p. 154—156°). On neutralisation of the sulphuric acid

[10] Greenhow, McNeil, and White, *J.*, 1952, 986.
[11] Morgan and Walls, *J.*, 1931, 2450.

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solution 9-methylphenanthridine (440 mg.), m. p. 82—84°, was obtained. From a second experiment in which the addition was made during 10 min. the yields were: infusible solid (190 mg.), (9-methyl-9-fluorenyl)-9-phenanthridinylmethane (70 mg.), m. p. 152—156°, and 9-methylphenanthridine (520 mg.), m. p. 84°.

(9-*Azido*-9-*fluorenyl*)-(9-*methyl*-9-*fluorenyl*)*methane*.—(a) *From* 9-*methylfluoren*-9-*ol*. 9-Methyl-fluoren-9-ol (2·0 g.), trichloroacetic acid (10 g.), chloroform (10 ml.), and sodium azide (1·3 g.) were stirred together at 30° for 2 hr., then poured into water. The organic layer afforded, as above, a yellow oil which partly crystallised. The crystals (0·66 g.) were collected, washed with light petroleum, and recrystallised from ethanol (50 ml.). (9-*Azido*-9-*fluorenyl*)-(9-*methyl*-9-*fluorenyl*)*methane* formed tablets (0·40 g.), m. p. 140° (Found: C, 83·9; H, 5·5; N, 9·9. $C_{28}H_{21}N_3$ requires C, 84·2; H, 5·3; N, 10·5%).

(b) *From* (9-*hydroxy*-9-*fluorenyl*)-(9-*methyl*-9-*fluorenyl*)*methane*. This alcohol (22 mg.) was added during 10 min. to a stirred mixture of trichloroacetic acid (200 mg.), chloroform (0·2 ml.), and sodium azide (30 mg.) at 25°. After a further 1½ hr. water and more chloroform were added, and the organic layer was separated, washed with water, and evaporated, yielding a crystalline mass (20 mg.), m. p. 138—139°. Recrystallisation of this azide from ethanol (1 ml.) gave needles (16 mg.), m. p. and mixed m. p. 139—140°.

This azide (1·0 g.) was treated with hydrazoic and sulphuric acid in chloroform, as described for 9-azido-9-methylfluorene (above). The white solid that separated when the mixture was poured into water was collected; it (0·40 g.) was infusible and insoluble in the usual organic solvents. The aqueous and the chloroform layer were separated. The latter, on evaporation, gave a brown solid (0·55 g.), which was infusible and insoluble in ethanol.