ALIPHATIC CHEMISTRY OF FLUORENE

PART II. AN UNUSUAL GRIGNARD REACTION[1]

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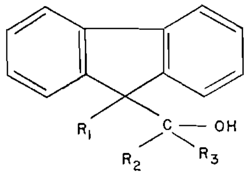
ABSTRACT

The reaction between methyl 9-methylfluorene-9-carboxylate and phenyl magnesium iodide gave 9,9′-dimethyl-9,9′-difluorenyl in almost quantitative yield. Evidence is presented which shows that 9-methylfluorene anion is an intermediate. The probable intervention of elemental iodine is discussed.

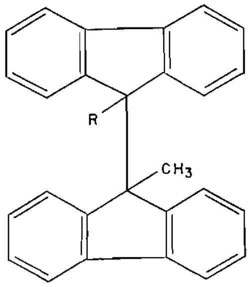
9-Methyl-9,9′-difluorenyl and 9,9′-dimethyl-9,9′-difluorenyl have been synthesized. A convenient preparation of 9,9′-difluorenylidene is described.

Some years ago we were interested in the reaction between phosphorus pentoxide and tertiary alcohols having structure I, where R is not hydrogen (1). We succeeded in preparing only two alcohols of the desired structure (I, $R_1 = R_2 = R_3$ = methyl or ethyl) by the reaction between methyl 9-methyl or ethylfluorene-9-carboxylate and the corresponding alkyl magnesium halide. The similar reaction between methyl 9-methylfluorene-9-carboxylate and phenyl magnesium bromide gave an easily crystallized hydrocarbon of melting point 209–210°, which has now been identified as 9,9′-dimethyl-9,9′-difluorenyl (II*b*). Although this hydrocarbon has been reported previously (2, 3, 4) identity has been established by the following unambiguous syntheses.

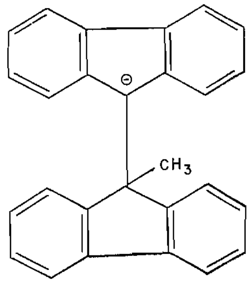
9-Bromofluorene reacted rapidly with methyl fluorene-9-carboxylate anion to give methyl 9-(9′-fluorenyl)-fluorene-9-carboxylate (the ethyl ester has been prepared previously from 9,9′-difluorenyl (5)), which was saponified and decarboxylated to 9,9′-difluorenyl. Methylation with methyl lithium and methyl iodide gave finally 9,9′-dimethyl-9,9′-difluorenyl (II*b*).



(I)



(II)



(III)

(a) R = H
(b) R = CH_3

In the second synthesis, the anion (III) was prepared by the addition of methyl lithium to 9,9′-difluorenylidene. The further reaction with methyl iodide gave 9,9′-dimethyl-9,9′-difluorenyl. The preparation of 9-methyl-9,9′-difluorenyl (II*a*) by hydrolysis of the anion (III) with water proved unexpectedly difficult, residual methyl iodide giving

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[1] *Manuscript received December 1, 1959.*
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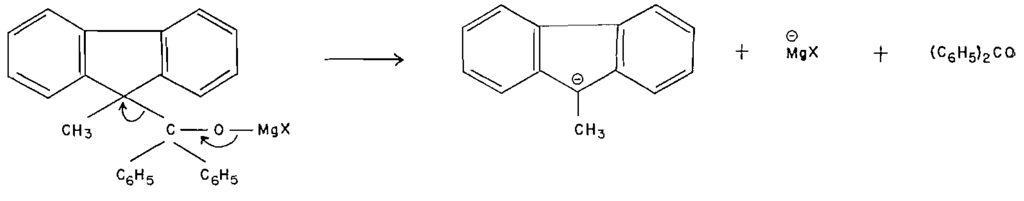
instead dimethyldifluorenyl (II*b*). After removing the last traces of methyl iodide with magnesium, 9-methyl-9,9′-difluorenyl was obtained in 80–90% yield.

The yield of the hydrocarbon (II*b*) in the Grignard reaction was almost quantitative when phenyl magnesium iodide was used, from which it was inferred that the tertiary alkoxide (IV) was formed in the usual way. By analogy with certain tertiary aliphatic alkoxides recently investigated by Zook (6), decomposition should lead to 9-methylfluorene anion (V) and benzophenone, as shown in the annexed scheme (Fig. 1). The necessary driving force for the decomposition is supplied by the mesomeric nature of the ion (V) (cf. the facile base-induced cleavage of 9-methyl-9-benzoylfluorene (7)), which accounts for the unusually low reaction temperature (cf. (6)).*



(IV) (V)

FIG. 1.

The use of organic iodides in the preparation of Grignard reagents, or of a crystal of iodine to initiate their formation, may often result in the presence of traces of free iodine in such reactions, probably owing their formation to aerial oxidation. It is well known that iodine brings about the dimerization of many esters in the presence of strong base (e.g. phenylacetic ester (8)) and, by analogy, it might be expected to bring about dimerization of the anion (V) to dimethyldifluorenyl (II*b*).

Evidence is presented below which supports the postulated decomposition of the tertiary alkoxide (IV) and the participation of iodine in the formation of the hydrocarbon (II*b*).

Evidence for the Formation of the 9-Methylfluorene Anion (V)

The most convincing evidence for the formation of the anion (V) came from a study of the reactions of 9-methyl-9-benzoylfluorene, which has recently been prepared for the first time (7). The ketone reacted with ethereal methyl or phenyl lithium and with ethereal phenyl magnesium bromide to produce a deep red color, which was fully developed in a few minutes. In order to demonstrate the presence of the anion (V), methyl iodide was added. 9,9-Dimethylfluorene could then be isolated from amongst the products. Triphenylmethanol could be isolated from the products of reaction with phenyl lithium or the corresponding Grignard reagent, thereby accounting for the benzophenone formed in the decomposition of the tertiary alkoxide (IV). Prolonged reaction times favored formation of the hydrocarbon (II*b*). Other experiments showed that methyl 9-methylfluorene-9-carboxylate gave the same products under the same conditions.

It is probable that the formation of the anion (V) from the ketone proceeds by way of the tertiary alkoxide (IV), but it may equally well involve base-induced cleavage of the non-enolizable ketone (7), with methyl or phenyl anion acting as base. Similar

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**Zook (6) has emphasized that the decompositions are the reversal of addition of an organometallic reagent to a ketone.*

mechanisms can account for the formation of acetophenone and triphenylmethane from the reaction between benzopinacolin and methyl magnesium bromide (reference 3 quoted in 6). In both cases the direction of cleavage is controlled by formation of the mesomeric ions (V) and the triphenylmethyl anion. Differentiation between the decomposition and cleavage mechanisms might be possible by kinetic studies.

The Role of Iodine

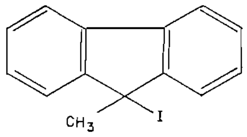
The importance of iodine may be judged from the following experimental results.

(i) The yield of the hydrocarbon (II*b*) from methyl 9-methyl-fluorene-9-carboxylate was almost quantitative when phenyl magnesium iodide was used, but was considerably less with phenyl magnesium bromide.

(ii) The anion (V), generated from 9-methylfluorene with phenyl lithium, reacted rapidly with iodine to give a good yield of the hydrocarbon (II*b*). Under similar conditions fluorene gave 9,9′-difluorenyl.

(iii) The reaction between 9-methylfluorene, ethyl lithium, and ethyl iodide produced 10% of the hydrocarbon (II*b*). The similar reaction using ethyl bromide and ethyl lithium prepared from ethyl bromide gave only 9-ethyl-9-methylfluorene.

Since many Grignard reagents react with iodine to give good yields of iodides (9, pp. 1332–1335) the tertiary iodide (VI) has to be considered as a possible intermediate in the formation of the hydrocarbon (II*b*) by reaction with the anion (V). Evidence for the formation of a reactive iodo compound in the dimerization of phenylacetic ester has already been reported (8, footnote on page 446; see also 10), and it has now been observed that traces of unstable iodo compounds are present in the products of the dimerization of fluorene or 9-methylfluorene with iodine and phenyl lithium.



(VI)

Tertiary halides do not as a general rule give C-alkylation products with organic anions. However, methyl fluorene-9-carboxylate anion has been shown to be exceptional in this respect (11, 12). It has now been found that methyl 9-bromofluorene-9-carboxylate reacts rapidly with methyl fluorene-9-carboxylate anion to give dimethyl 9,9′-difluorenyl-9,9′-dicarboxylate, at a rate comparable with that observed for the iodine-induced dimerization of the anion. These results suggest the feasibility of the anion (V) reacting with the iodide (VI) to give II*b*.

Comparable experiments with 9-bromo-9-methylfluorene and methyl fluorene-9-carboxylate anion have been unsuccessful. Crude preparations of the bromide, difficult to obtain pure (30), gave a low yield of what is probably methyl 9-(9′-fluorenylmethyl)-fluorene-9-carboxylate as the product of Michael addition of methyl fluorene-9-carboxylate anion to 9-methylenefluorene. Experiments with the corresponding chloride, which has not been obtained pure (13, 30), gave similar results.

Alternative mechanisms for the formation of the hydrocarbon (II*b*) obviously cannot be ruled out. For example, oxidation of the anion (V) by iodine might give the radical, leading by dimerization to II*b*. In addition, trace amounts of certain metals are known to bring about oxidative coupling of organic anions (9).

Summing up the available evidence, it is clear that formation of dimethyldifluorenyl (II*b*) in the reaction between methyl 9-methylfluorene-9-carboxylate and a phenyl Grignard reagent proceeds through 9-methylfluorene anion (V), formed either by decomposition of the tertiary alkoxide (IV) or by basic cleavage of 9-methyl-9-benzoylfluorene. Iodine seems to play an essential part but its exact role is uncertain.

The formation of 9,9′-difluorenyl by the reaction between Grignard reagents and 9-chlorofluorene (14) may very well be related to its formation from fluorene, phenyl lithium, and iodine, mentioned above. The annexed scheme (Fig. 2) shows the reactions likely to be involved. It will be seen that an essential postulated reaction is a Grignard exchange having forward rate k_2. The existence of at least two such reactions has been convincingly demonstrated (15, 16) but it has been claimed that 9-chlorofluorene does not exchange with methyl magnesium bromide (17) because fluorene-9-carboxylic acid was not isolated from amongst the products of carbonation. These workers seem to have been unaware of the earlier paper by Bachmann (14); neglect to report on the neutral products obviously invalidates their work. The reaction between 9-bromofluorene and methyl magnesium iodide has been found to give 9,9′-difluorenyl in more than 90% yield, even in the presence of added methyl iodide. This observation confirms Bachmann's results (14).

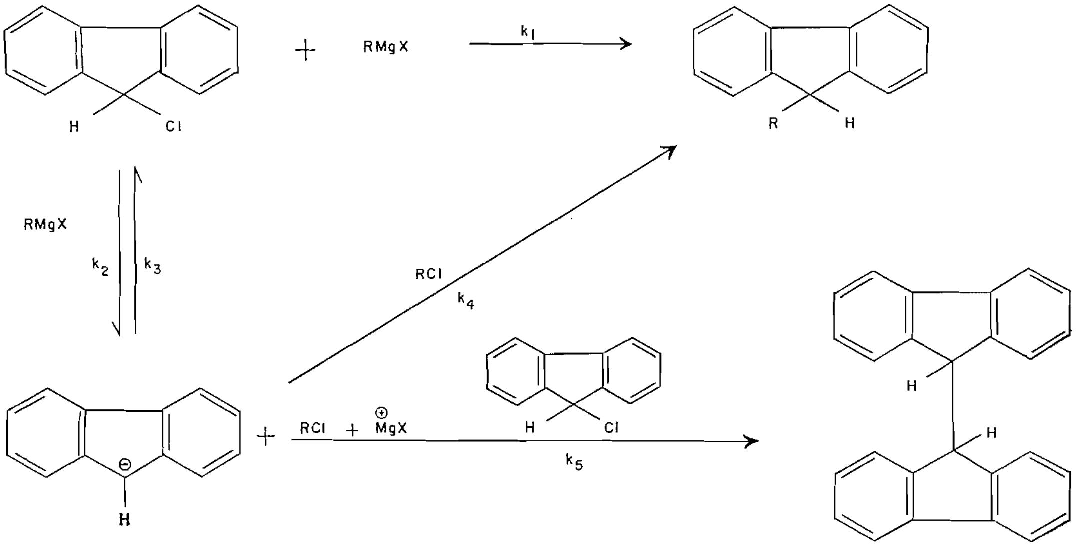


FIG. 2.

Bachmann's efforts to explain his results (14), particularly the infrequent formation of 9-alkylfluorenes, in terms of the structure of the Grignard reagent are almost certainly invalid in view of recent studies with the ^{28}Mg isotope (18). The alternative scheme shown in Fig. 2 may provide a complete explanation. The rate k_1 is likely to be small compared with k_2 so that *the products formed will depend on the reactivities of 9-chlorofluorene and the halide RCl towards fluorene anion*, the reactivities being measured by k_5 and k_4.

An outstanding property of fluorene anions is the speed with which they react with a very wide range of alkyl halides (7, 11, 12). It has now been demonstrated that the anions from fluorene, 9-methylfluorene, and 9-phenylfluorene react almost instantaneously with methyl iodide, providing convenient preparations of 9,9-dimethylfluorene and 9-methyl-9-phenylfluorene. The relative reactivities of various alkyl halides to methyl fluorene-9-carboxylate anion are being measured by competition and will be reported later. The formation of difluorenyl from the reaction between 9-bromofluorene and methyl Grignard in the presence of methyl iodide suggests that the fluorene halide is the more reactive.

The reaction between 9-bromofluorene and sodium *t*-butoxide has been found to give 9,9′-difluorenylidene in 85% yield, representing a considerable improvement in both yield and convenience over published preparations (20, 21).

The existence (19) has been confirmed of two polymorphic forms of 9,9-dimethylfluorene.

EXPERIMENTAL

9,9′-Dimethyl-9,9′-difluorenyl (II*b*)

(i) Methyl 9-methylfluorene-9-carboxylate (2.24 g, 0.01 mole) was boiled under reflux for 4 hours with ethereal phenyl magnesium iodide (from iodobenzene, 12 g, 0.06 mole). The complex was decomposed with ice and ammonium chloride and the product crystallized from heptane to give pale yellow prisms, m.p. 186–190° (1.76 g, almost quantitative yield). Two further crystallizations yielded colorless well-defined rhombs (1.6 g), m.p. 209–210°. Found for two samples: C, 93.71, 93.97; H, 6.29, 6.19%. Calculated for $C_{28}H_{22}$: C, 93.81; H, 6.19% (lit. m.p.: 209° corr. (2), 209–210° (3), 205° (4)).

Phenyl magnesium bromide was used in earlier experiments, formation of the Grignard reagent being assisted by the addition of a crystal of iodine. The hydrocarbon (II*b*) was obtained in 45% yield only after 24 hours. In the absence of iodine the hydrocarbon was not formed.

(ii) 9-Bromofluorene (22), prepared by Bolton, reacted rapidly at 30–35° with one equivalent of methanolic methyl fluorene-9-carboxylate anion. *Methyl 9-(9′-fluorenyl)-fluorene-9-carboxylate*, isolated in the usual way, formed well-defined rhombs (76%) from benzene–hexane, m.p. 215–216°. Found: C, 86.11; H, 5.18%. Calculated for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19%.

The ester was boiled under reflux for 2 hours with twice its weight of potassium hydroxide in ethylene glycol. Cooling and diluting with water precipitated 9,9′-difluorenyl, which crystallized as slender colorless needles (94%) from benzene–hexane, m.p. 248–249°.

9,9′-Difluorenyl (2 g) in benzene (200 ml) was added to ethereal phenyl lithium (from bromobenzene, 20 g) to give a deep red solution, the color of which was almost instantly discharged on addition of methyl iodide (8 g). The *hydrocarbon* crystallized as rhombs (1.4 g) from benzene–hexane, m.p. 209–210°. Identity with the product from (i) was established by mixed melting point determination and comparison of infrared spectra.

(iii) 9-Methylfluorene (1 g) was added to ethereal phenyl lithium (from bromobenzene, 5 g) followed by crystals of iodine until the color of the latter persisted. The product (0.8 g) had a melting point of 207–209° and was identical with that obtained from (i).

Under similar conditions fluorene (1 g) gave 9,9′-difluorenyl (0.7 g), m.p. and mixed m.p. 245–246°.

The crude products from both preparations were washed with a solution of sodium metabisulphite to remove iodine, but traces of the latter were always formed during crystallization.

(iv) 9,9′-Difluorenylidene (1 g) was boiled under reflux for 30 minutes with ethereal methyl lithium (from methyl iodide, 10 g) and methyl iodide (10 g). The product crystallized from heptane as small colorless prisms (0.9 g), m.p. 208–210°, and was identical with the product from (i).

9,9′-Difluorenylidene

A hot solution of sodium *t*-butoxide (from sodium, 7 g) in *t*-butanol (500 ml) was added to 9-bromofluorene (25 g) and the mixture boiled under reflux for 15 minutes. Most of the solvent was recovered by distillation and the residue poured into dilute hydrochloric acid (500 ml). The reddish-orange solid was collected, washed with water, dried, and crystallized from carbon tetrachloride – ethanol, which was the best solvent system found. Difluorenylidene was obtained as beautiful red needles (14.2 g, 85%, in two crops), m.p. 187–189° (lit. m.p. 185–187° (20, 21)).

9-Methyl-9,9′-difluorenyl

Ethereal methyl lithium was prepared from methyl iodide (28 g) and lithium (3 g). When the reaction was apparently complete, magnesium (5 g) was added and the mixture boiled gently under reflux for 30 minutes. Residual solids were removed by decantation through a plug of glass wool to give a solution of methyl lithium in ether free from methyl iodide.

Difluorenylidene (1 g) was warmed for 15 minutes with an excess of the above methyl lithium reagent. The ether layer was washed with water, dried, and evaporated, leaving the product as a yellow solid. The product was purified by passing a hexane solution through a column of activated alumina, crystallization of the eluted material from heptane yielding small colorless prisms (0.85 g), m.p. 169–170° (lit. m.p. 172° (4)). Found: C, 94.25; H, 5.89%. Calculated for $C_{27}H_{20}$: C, 94.15; H, 5.85%.

A mixed melting point determination with dimethyldifluorenyl was 151–179°.

9-Ethyl-9-methylfluorene

(i) 9-Methylfluorene (1 g) was added to ethereal ethyl lithium (from ethyl bromide, 4 g), followed by ethyl bromide (4 g). The product crystallized readily from methanol as white needles (0.8 g), m.p. 59–60.5° (lit. m.p. 61–62° (23)).

(ii) Ethyl iodide replaced ethyl bromide in (i). Crystallization of the product from heptane gave small colorless prisms (0.1 g), m.p. 204–207°, identified as 9,9′-dimethyl-9,9′-difluorenyl. The mother liquors contained impure ethylmethylfluorene.

9,9-Dimethylfluorene

(i) Fluorene (16.6 g, 0.1 mole) was added to ethereal methyl lithium (from methyl iodide, 43 g, 0.3 mole). Methyl iodide was added dropwise until the solution became colorless. The product crystallized from methanol as colorless prismatic needles (17.3 g, 89%), m.p. 90–93°, raised to 95–96° by a further crystallization.

Phenyl lithium gave less satisfactory yields unless the product was distilled at 1 to 2 mm prior to crystallization.

(ii) Methylation of 9-methylfluorene with methyl lithium – methyl iodide gave, in the same way, 9,9-dimethylfluorene in 92%.

Two melting points have been recorded for 9,9-dimethylfluorene: 71° (19) and 69–70° (24), 95–96° (19, 25) and 96° (23). Through the kindness of Dr. C. C. Barker, his original sample (24) has been examined after a lapse of several years and found to have a melting point of 81–92°, raised to 95–96° by one crystallization from methanol. Attempts by Emmerson (24) to obtain the higher melting form had been unsuccessful but the present author has been unable to obtain the lower melting form. The existence of the two crystalline forms reported earlier (19) is thus confirmed.

9-Methyl-9-phenylfluorene

Methylation of 9-phenylfluorene as described for fluorene gave methylphenylfluorene in 87% yield, crystallizing as colorless lustrous plates from methanol, m.p. 86–86.5° (lit. m.p. 84–85° (26), 86–87° (27)). Found: C, 93.97; H, 6.19%. Calculated for $C_{20}H_{16}$: C, 93.71; H, 6.29%.

Experiments with 9-Methyl-9-benzoylfluorene

(i) 9-Methyl-9-benzoylfluorene (2 g) in dry ether (100 ml) was added to ethereal phenyl lithium (from bromobenzene, 5 g). The solution immediately assumed a deep red color, similar to that produced by adding 9-methylfluorene to phenyl lithium. The color was rapidly discharged by the addition of methyl iodide (2 g). The product crystallized from methanol as colorless prismatic needles (0.9 g), m.p. 94–96°, identified as 9,9-dimethylfluorene. Found: C, 92.46; H, 7.04%. Calculated for $C_{15}H_{14}$: C, 92.74; H, 7.26%.

(ii) The experiment was performed as in (i) but without the addition of methyl iodide. The product crystallized as long needles (0.17 g) from methanol, m.p. 163–164°, after several crystallizations. Found: C, 87.43; H, 6.13%. Calculated for $C_{19}H_{16}O$: C, 87.66; H, 6.20%. Identity with triphenylmethanol was established by mixed melting point determination and comparison of infrared spectra. The oily residues were not examined.

In other experiments, methyl 9-methylfluorene-9-carboxylate satisfactorily replaced the ketone, and methyl lithium replaced phenyl lithium, although attempts were not made to isolate methyldiphenylmethanol.

9,9′-Difluorenyl

Ethereal methyl magnesium iodide (from methyl iodide, 4 g) was decanted from magnesium and added dropwise to a solution of 9-bromofluorene (2.4 g) and methyl iodide (2 g) in ether. After 10 minutes, the complex was decomposed with ice and ammonium chloride. The product was crystallized from heptane to give, in two crops, difluorenyl (1.5 g), m.p. and mixed m.p. 244–246°.

Dimethyl 9,9′-difluorenyl-9,9′-dicarboxylate

Methyl 9-bromofluorene-9-carboxylate (1.3 g) was added to a solution of methyl fluorene-9-carboxylate (1 g) in methanol containing sodium methoxide (from sodium, 0.2 g) and the suspension was warmed for 10 minutes. The product crystallized as small prisms (1.1 g) from benzene–hexane, m.p. 238–240°, identical with a sample prepared by the reaction between methyl fluorene-9-carboxylate anion and iodine (cf. 29) (lit. m.p. 237° (28)).

Methyl 9-(9′-fluorenylmethyl)-fluorene-9-carboxylate (?)

9-Methyl-9-fluorenol (1 g) was warmed for a few minutes with dry ether (30 ml) and acetyl bromide (1 ml). The solvent was evaporated below 30° and to the residual oil was added a solution of methyl fluorene-9-carboxylate (1.1 g) in methanol (30 ml) containing sodium methoxide (from sodium, 0.2 g). Polymeric material was removed by filtration, after which the clear yellow filtrate was warmed for 30 minutes. Careful dilution with water and scratching induced crystallization. After two crystallizations from heptane the colorless prisms (0.2 g) had a melting point of 173–174°. Found: C, 85.97; H, 6.16%. Calculated for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51%.

Saponification in ethylene glycol was incomplete after 2 hours and yielded an unresolved mixture from which 9-methyl-9,9′-difluorenyl was not obtained by seeding, although a careful comparison of infrared spectra suggested its presence.

ACKNOWLEDGMENTS

The author is indebted to Professor N. B. Chapman for his interest and encouragement, to Doctors K. Clarke and J. Parrick for commenting on the manuscript, and to Dr. G. W. Gray and Miss A. Stephenson for the infrared spectra. Mr. R. Bolton kindly provided details of unpublished work on the 9-halo-9-methylfluorenes.

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