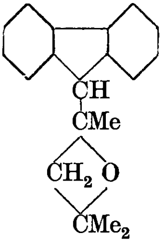
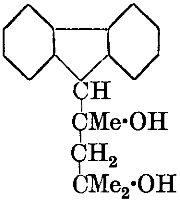
CCCXLII.—*The Condensation of Fluorene with Acetone. Part I. The Action of Magnesium* 9-*Fluorenyl Bromide on* (a) *Acetone,* (b) *Diacetone Alcohol. The Question of Two Forms of* 9-iso*Propylidenefluorene.*

By Peter Maitland and Stanley Horwood Tucker.

Fluorene reacts with acetone in the presence of potassium hydroxide to give a compound, $C_{19}H_{20}O$, m. p. 76—78°, the preparation of which will be described in a subsequent communication. It was at first thought that this compound contained an ethereal oxygen atom and might be formulated as (I).


(I.)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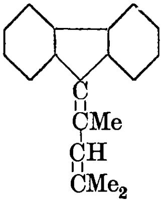
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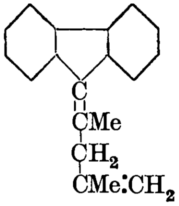

(IV.)

On this idea a synthesis was attempted from magnesium 9-fluorenyl bromide and diacetone alcohol to obtain (after the usual treatment) the compound (II), which should readily be converted directly, or *via* the chlorohydrin, into (I). The compound (II) was actually isolated in small yield, but it has not yet been converted into (I), because this structural formula for the compound $C_{19}H_{20}O$ has been abandoned. The work now to be described has, however, a direct bearing on the structure of the compound $C_{19}H_{20}O$, as will be shown in a subsequent communication.

The action of magnesium 9-fluorenyl bromide on diacetone alcohol gives rise to several products: (a) *α-9-fluorenyl-αγγ-trimethyltrimethylene glycol* (II), m. p. 110—112°; (b) a phototropic *substance*, $C_{19}H_{18}$, m. p. 80—82°; (c) a *substance*, $C_{19}H_{18}$, m. p. 58—61°; and (d) 9-fluorenyldimethylcarbinol, m. p. 99—101° (Courtot, *Ann. Chim.*, 1915, **4**, 162, gives m. p. 103°).

In the above reaction half of the fluorene used should be recovered unchanged as the result of the action of the Grignard reagent on the hydroxyl group. Much more than half was recovered. The yields of the above substances were very small and a considerable amount of uncrystallisable oil was obtained. The first product of the reaction would appear to be the glycol (II), but this was isolated on one occasion only and then in sufficient quantity for analysis only. It seems to be almost impossible to prevent this compound from losing water by the action of the Grignard reagent, giving oils from which nothing crystalline can be obtained. To prepare appreciable quantities of the products (b)—(d) it was necessary to work under conditions which brought about the destruction of (a) with elimination of water. Thus was obtained (b), which may be α-diphenylene-βδ-dimethyl-$\Delta^{\alpha\delta}$-pentadiene (IV), or more probably (as will be shown in another communication) α-diphenylene-βδ-dimethyl-$\Delta^{\alpha\gamma}$-pentadiene (III). Reduction of the compound (III or IV) gave a saturated hydrocarbon, $C_{19}H_{22}$, m. p. 101—103°, which will therefore be β-9-*fluorenyl*-δ-*methylpentane.*

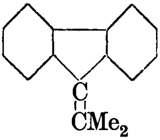
The substance (c) is possibly the isomeride of (b) represented by (III) or (IV). The quantity obtained was too small for investigation.

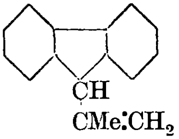
The remaining substance (d) is probably the product of the direct action of magnesium 9-fluorenyl bromide on acetone, either originally contained in admixture with the diacetone alcohol or formed from it during the reaction (see later, under condensation of magnesium 9-fluorenyl bromide with acetone). It is well known that diacetone alcohol, when kept in the presence of a base, decomposes into acetone until an equilibrium mixture is obtained (Koelichen, *Z. physikal. Chem.*, 1900, **33**, 129).

The action of magnesium 9-fluorenyl bromide on acetone has been studied by Courtot (*loc. cit.*, p. 161), who obtained 9-fluorenyldimethylcarbinol (" dimethyldibenzofulvanol "), m. p. 103°, in low yield. We have been able to obtain (i) this compound, m. p. 99—101°, in 50% yield, calculated on the unrecoverable fluorene used; (ii) the substance, m. p. 58—61°, listed as (c) on p. 2559; (iii) 9-*iso*-propylidenefluorene (V), m. p. 113—117°; and (iv) 9 : 9′-difluorenyl. The products (ii) and (iv) were isolated in small quantities, but (iii) was sometimes the main product of the reaction.

Courtot prepared 9-*iso*propylidenefluorene (" dimethyldibenzofulvene "; *loc. cit.*, p. 220) by heating 9-fluorenyldimethylcarbinyl chloride with pyridine and described it as a light yellow substance melting at 89°. We repeated Courtot's work and obtained 9-*iso*-propylidenefluorene, by slow distillation in steam or crystallisation from alcohol or ligroin (b. p. 60—80°), as colourless needles softening at 110° and melting at 113—117°. We were also able to prepare the same compound from magnesium *iso*propyl bromide and fluorenone, thus providing strong evidence that the position of the double bond is as shown in (V) and not as in (VI).

(V.)





(VI.)

We communicated these results to Professor Courtot on July 6th, 1928, before the publication of a paper by Schlenk and Bergmann (*Annalen*, 1928, **463**, 207, 215), who prepared 9-*iso*propylidenefluorene from magnesium 9-*iso*propyl chloride and fluorenone and gave the melting point as 113°; but they could neither prepare this compound by Courtot's method nor obtain the compound, m. p. 89°, described by Courtot. Furthermore, they describe the former as an unstable yellow compound which soon becomes brown and viscous. The compound obtained by us is stable in the dark, but becomes yellow and soft when exposed to light. A paper containing these results was submitted to the Chemical Society on August 1st, 1928 (P., 1928, 91), but has not yet been published.

No compound corresponding to that, m. p. 89°, described by Courtot could be isolated by us; and we therefore consider that the statement of Schlenk and Bergmann (*loc. cit.*, p. 207), "Wir halten es zwar für sehr wahrscheinlich, dass es sich hier um Stereoisomere in dem oben gekennzeichneten Sinne handelt" is untenable, since it is based on the doubtful existence of the compound of alleged m. p. 89°.

For future synthetic work, 9-fluorenyldimethylcarbinyl chloride and bromide were prepared from 9-fluorenyldimethylcarbinol, but attempts to convert them into the iodide by the action of sodium iodide in acetone (Finkelstein, *Ber.*, 1910, **43**, 1528) were fruitless. The action of sodium iodide in alcohol and in acetic acid gave peculiar results, needing further study.

9-iso*Propylfluorene* has been prepared (*a*) by the reduction of 9-*iso*propylidenefluorene (V), and (*b*) from the potassium derivative of 9-carbethoxyfluorene and *iso*propyl iodide, followed by hydrolysis and removal of carbon dioxide from the carboxylic acid.

EXPERIMENTAL.

Magnesium 9-Fluorenyl Bromide.—The method of Courtot * (*loc. cit.*, p. 84) was followed, with important variations. Magnesium ethyl

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* We are grateful to Professor Courtot for furnishing helpful information relating to the preparation of magnesium 9-fluorenyl bromide.

bromide was prepared in the usual way from magnesium (12 g.), ethyl bromide (48 c.c.), and ether (200 c.c.) with vigorous stirring (Gilman and Meyers, *J. Amer. Chem. Soc.*, 1923, **45**, 159). Fluorene (84 g.) and xylene (250 c.c.) were added and the mixture was heated in a glycerol bath, stirring being continued throughout the whole experiment. (The stirrer, turning in a mercury seal, was driven at a high speed by means of an electric motor.) Ether slowly distilled, and when the temperature had reached 136—137° (bath temperature, that of the liquid being 2—3° lower) most of it had passed over, leaving a clear green liquid. This took 1 hour; after a further ½ hour, white nodules (magnesium ethyl bromide) began to separate. (It is essential to remove all the ether; and, accordingly, the condenser was kept attached to a receiver throughout the subsequent period of heating.) The liquid was maintained *strictly* at 136—137° for a further 12 hours, every care being taken to prevent the entry of moisture. The nodules were, finally, pale green (magnesium 9-fluorenyl bromide), and practically filled the enclosing red liquor (compare Courtot, *loc. cit.*, p. 84). The period of heating (12 hours) may be discontinuous.

The Action of Acetone on Magnesium 9-*Fluorenyl Bromide. Preparation of* 9-*Fluorenyldimethylcarbinol* (compare Courtot, *loc. cit.*, p. 161).—Acetone (38 c.c., approximately the theoretical quantity; which had been dried over anhydrous sodium sulphate, and distilled just before use) was added dropwise, with very vigorous stirring, during 1½ hours to the magnesium 9-fluorenyl bromide prepared as above, and immersed in ice. The nodules turned from pale green through pale brown to a white pasty-looking solid. Stirring, at room temperature, was continued for ½ hour. The mixture was then heated in a glycerol bath to 125°.* After 5 minutes at this temperature the white paste changed to a thin suspension of pale brown, gelatinous particles; at the end of a further 10 minutes' heating, the whole suddenly set to a thick, slightly yellow paste. Heating was continued for 1 hour. (The temperature must on no account rise above 125°. Also, stirring must, throughout, be very vigorous, to prevent the gelatinous particles from coalescing.) The cooled mixture was poured into dilute sulphuric acid, the xylene layer separated, the aqueous portion extracted once with ether, and the united xylene–ether extracts washed twice with equal volumes of water and distilled without drying. After ether and most of the xylene had been removed, the residue was distilled under reduced pressure. (The pressure must be reduced before darkening and crackling—due to liberation of water with attendant decomposition of the desired carbinol—commence.) Fractions were collected

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* The reaction which takes place at 135° is considered on p. 2563.

(13—15 mm.) at (i) 75°, a pleasant-smelling liquid (3 g.), which was not investigated; (ii) 155—165°, fluorene (22—26 g.); (iii) 165—185°, a mixture of fluorene and 9-fluorenyldimethylcarbinol (about 45 g.); (iv) 185—215° (chiefly at 193°, and only a small amount above 205°), a mixture (35—41 g.) containing a large proportion of the carbinol with oil but no fluorene. The residue (3—5 g.) in the flask consisted of 9 : 9′-difluorenyl, m. p. 246—247°. From an alcoholic solution of fraction (iii), fluorene (30 g.), m. p. 115°, separated practically completely on cooling; the filtrate was evaporated to dryness and the slightly oily residue was pressed on porous plate and crystallised from ligroin (b. p. 60—80°), giving the carbinol (6—9 g.). Fraction (iv), crystallised from ligroin (b. p. 60—80°), gave the carbinol (18—20 g.); the filtrate on evaporation left a yellow, uncrystallisable oil (15—20 g.). The total amount of carbinol (24—29 g.) obtained represents 20—25% of the theoretical yield, or 50—60% calculated on *unrecovered* fluorene. 9-Fluorenyldimethylcarbinol crystallises from ligroin, or from a very concentrated solution in alcohol, in large colourless rhombs, m. p. 99—101° (Found:* C, 85·8; H, 7·1. Calc.: C, 85·7; H, 7·1%). It possesses slight vesicant and sternutatory properties.

In experiments in which the temperature of heating was 135°, instead of 125°, no carbinol could be isolated, but treatment as above gave a fraction, b. p. 185—230°/15 mm., which after crystallisation from alcohol gave 9-*iso*propylidenefluorene (3 g.) (see later). From the alcoholic filtrate a substance was obtained which, after ten crystallisations from methyl alcohol, separated in wheat-sheaf clusters of colourless needles; these, alone or mixed with the substance described on p. 2565, melted at 58—61°.

9-*Fluorenyldimethylcarbinyl bromide* was prepared by passing dry hydrogen bromide into a solution of 9-fluorenyldimethylcarbinol in cold alcohol or glacial acetic acid (Found: Br, 27·6. $C_{16}H_{15}Br$ requires Br, 27·9%). Recrystallisation from alcohol, glacial acetic acid, or ligroin (b. p. 60—80°) did not alter the m. p., 98—103°. This cannot, however, be taken as indicative of the purity of the substance, since the melting points (*e.g.*, 70°) of crude specimens of this substance were unaffected by recrystallisation.

By heating 9-fluorenyldimethylcarbinyl chloride at 180°, 9-*iso*propylidenefluorene, m. p. 113—117°, was produced and also a compound, m. p. 50—59°, which is being investigated.

Synthesis of 9-iso*Propylidenefluorene.*—To the reagent prepared from magnesium (2·4 g.) and *iso*propyl bromide (12·3 g.) in dry

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* Analyses recorded in this paper were performed with a tube containing a mixture of copper oxide and lead chromate (Pregl, "Die quantitative organische Mikroanalyse").

ether (50 c.c.), fluorenone (18 g.) in ether was added slowly. At the end of the reaction the solution was heated on a water-bath for ½ hour, cooled, and poured into ice and hydrochloric acid. The ethereal extract gave an oil, of which the portion distilling below 200°/15 mm. was crystallised from ligroin. The first and second crops were fluorenone; the third crop formed long needles, which were recrystallised from alcohol, and proved to be 9-*iso*propylidenefluorene.

Bromine Addition Product of 9-iso*Propylidenefluorene.*—The pure compound (0·7 g.) was dissolved in carbon disulphide (7 c.c.), and bromine (0·54 g.) in carbon disulphide (5·4 c.c.) added gradually with cooling; only a small amount of hydrogen bromide was evolved. After removal of the carbon disulphide in a current of air, the solid was crystallised twice from ligroin, 9-*bromofluorenyldimethylcarbinyl bromide* being obtained in slightly green prisms, which crushed to a white powder and melted at 126—127° to a green liquid (Found : Br, 43·3. $C_{16}H_{14}Br_2$ requires Br, 43·7%).

Attempts to prepare 9-fluorenyldimethylcarbinyl chloride by heating 9-*iso*propylidenefluorene with dry hydrogen chloride in glacial acetic acid under pressure for 3 hours at 150° were unsuccessful, the initial material being recovered.

9-iso*Propylfluorene.*—(a) *By reduction of* 9-iso*propylidenefluorene.* 9-*iso*Propylidenefluorene (2 g.) was boiled with hydriodic acid (*d* 1·700; 5 c.c.) in glacial acetic acid for 2 hours. After standing, needles separated which were insoluble in methyl or ethyl alcohol, but crystallised from glacial acetic acid in long needles, m. p. 235—240°, apparently consisting of 9 : 9′-difluorenyl (m. p. 245°). The filtrate from the reaction mixture gave, when poured into sulphurous acid, a pink solid which soon turned yellow. It crystallised from methyl alcohol, in which it was very soluble when hot, in long, pale yellow laminæ, m. p. 53—55°, of 9-iso*propylfluorene* (Found : C, 92·5; H, 7·8. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%). Distillation and subsequent crystallisation gave colourless laminæ.

(b) *By the action of* iso*propyl iodide on potassium 9-carbethoxyfluorene.* The ester (Wislicenus and Mocker, *Ber.*, 1913, **46**, 2779) (12 g.), dissolved in anhydrous ether (50 c.c.), was boiled with potassium (2 g.) until the metal had nearly all dissolved; complete solution was effected by addition of alcohol (2 g.). *iso*Propyl iodide (19 g., *i.e.*, more than twice the theoretical quantity) was then added. The mixture was heated on the water-bath, the ether evaporated, and the residue boiled for ½ hour with alcoholic sodium hydroxide in order to hydrolyse the ester produced by the above reaction. The solution was acidified with hydrochloric acid and the yellow solid which separated was washed, dried, and heated to expel carbon dioxide; the product was distilled and crystallised from alcohol, giving colourless laminæ of 9-*iso*propylfluorene.

Action of Diacetone Alcohol on Magnesium 9-Fluorenyl Bromide.—The Grignard reagent was prepared as described on p. 2562. To it, maintained at 110—120° and vigorously stirred, was added, dropwise, in the course of ¼ hour, freshly distilled diacetone alcohol (14·5 g., b. p. 76°/20 mm.). The greenish solid turned yellow, then brown and gelatinous (2 hours' stirring). The mixture was heated for 2 hours at 137° (bath temperature). After cooling, it was poured into very dilute sulphuric acid, the xylene layer removed, and the acid solution extracted once with ether. The combined extracts were washed with an equal volume of water and, without drying, concentrated by distillation to about 50 c.c.; the crystals then obtained were washed with cold alcohol and were practically pure fluorene (18—20 g.). The united filtrate and alcoholic washings, on evaporation and repetition of the above process, gave a further quantity of fluorene (5 g.). The filtrates were distilled. After all the xylene had passed over, the temperature of the liquid rapidly rose and violent crackling ensued, due obviously to liberation of water by decomposition of the material. Heating was continued until water had been removed, and the residual liquor was distilled under diminished pressure (15 mm.), fractions being collected (i) up to 170°, (ii) at 170—185°, (iii) at 185—225°, (iv) above 225° (difluorenyl). Fractions (i) and (ii) were crystallised from alcohol.

Fraction (i) (5·5 g.) contained fluorene (3·3 g.). In one experiment, the alcoholic filtrate from the fluorene gave, on slow evaporation, needles (2 g.) which, after distillation and several recrystallisations from alcohol and methyl alcohol, gave a *compound*, m. p. 58—61° (Found: C, 92·6, 92·6; H, 7·3, 7·3. $C_{19}H_{18}$ requires C, 92·7; H, 7·3%) (see also p. 2563). It was very soluble in cold carbon tetrachloride, ethyl acetate, acetone, or benzene and in warm glacial acetic acid, alcohol, ligroin, or methyl alcohol and scratching was necessary to start crystallisation.

Fraction (ii) (5 g.), by successive crystallisation from alcohol and ligroin, gave fluorene (1·5 g.). The filtrates therefrom gave 9-fluorenyldimethylcarbinol, which crystallised from ligroin (b. p. 60—80°) in large rhombs (1·3 g.), m. p. 99—101°.

Fraction (iii) (7 g.) was treated with excess of hot ligroin (b. p. 40—60°) and the solution together with the insoluble substance was kept and then filtered. Difluorenyl was thus removed. The oil left on evaporation of the filtrate was dissolved in alcohol; the solution deposited, after long standing (sometimes at once), colourless needles, which, after several recrystallisations from alcohol, softened at 80° and melted at 81—82° (yield, 0·2—0·5 g.) (Found:

C, 92·6; H, 7·4. $C_{19}H_{18}$ requires C, 92·7; H, 7·3%). This *substance* is soluble in ethyl or methyl alcohol or glacial acetic acid and very soluble in carbon tetrachloride, ethyl acetate, or benzene. It turns pink superficially after a few minutes' exposure to light, but becomes colourless again when kept in the dark for several days. Its solutions are colourless and are not affected by light. If left for long in the light, the pink crystals become brown and cannot then be reconverted into the colourless variety.

The evaporated filtrate from the substance of m. p. 80—82° gave an oil which crystallised from ligroin (b. p. 60—80°), giving another crop of 9-fluorenyldimethylcarbinol (0·8 g.), m. p. 99—101°.

Each fraction of the distillate left an uncrystallisable oil.

In one experiment, all the recovered fluorene was distilled under normal pressure. Fluorene and a small amount of oil were obtained. The whole was steam-distilled. The oily residue was crystallised from alcohol (giving fluorene), and the filtrate evaporated to an oil. This oil dissolved in ligroin (b. p. 40—60°) and *after some time*, by scratching, was deposited in crystals, m. p. 112°. These were almost insoluble in ligroin, but separated from a hot benzene solution, to which ligroin (b. p. 60—80°) had been added, in stellar clusters of *α-9-fluorenyl-αγγ-trimethyltrimethylene glycol* (II), m. p. 110—112° (Found: C, 80·6; H, 7·9. $C_{19}H_{22}O_2$ requires C, 80·8; H, 7·8%). This crystallised also from acetic acid or alcohol diluted with water. It was very soluble in ethyl acetate, acetone, and warm carbon tetrachloride and benzene.

Reduction of the Substance $C_{19}H_{18}$, m. p. 80—82° (III or IV).—The substance (1·5 g.), hydriodic acid (4·5 c.c.; *d* 1·700), and glacial acetic acid (50 c.c.) were boiled together for $\frac{3}{4}$ hour. Most of the acetic acid was distilled off, and sulphurous acid added until the liquid became pale cream in colour. The oil which separated was extracted by carbon tetrachloride, washed and dried, and the solvent removed by distillation. The residue was a pale green, blue-fluorescing oil. It dissolved in hot alcohol (about 5 c.c.) and, on cooling, large rhombs slowly separated (0·2 g.), melting after recrystallisation from ethyl or methyl alcohol at 101—103° (Found: C, 91·4; H, 8·5. *β-9-Fluorenyl-δ-methylpentane*, $C_{19}H_{22}$, requires C, 91·2; H, 8·8%). The filtrate from the above (0·2 g.), on standing over-night, deposited a crop (0·6 g.) which melted after several crystallisations from methyl alcohol at 51—55° (Found: C, 91·3; H, 8·4. $C_{19}H_{20}$ requires C, 91·9; H, 8·1%). The method of mixed melting points showed it to be different from the compound, m. p. 58—61° (p. 2565), and from 9-*iso*propylfluorene. It was very soluble in benzene or ligroin.

The authors gratefully acknowledge financial assistance from the Chemical Society and from the Government Grant Committee of the Royal Society. They also wish to express their indebtedness to Mr. James Cameron, who has performed the analyses recorded in this paper.

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[*Received, July* 1*st,* 1929.]