[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

1,9-CYCLOHEXYLENEFLUORENE, A PENTACYCLIC RING SYSTEM

CHARLES D. HURD AND JAMES D. MOLD[1]

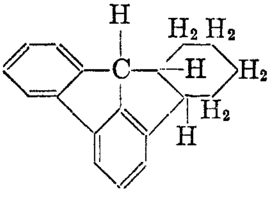
Received August 15, 1947

The present paper describes the synthesis of 1,9-cyclohexylenefluorene (I), which represents a new pentacyclic ring system. Dehydrogenation of this hydrocarbon gave rise to 9-phenylfluorene (II) instead of the expected 1,9-*o*-phenylenefluorene (III).

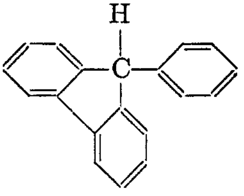
The first approach to the synthesis of III was by pyrolysis of 9-chloro-9-phenylfluorene at 260–270°. Hydrogen chloride was evolved, but III was not isolated. Instead, a dimeric product was formed in good yield. The equation:

$$2C_{19}H_{13}Cl \rightarrow C_{38}H_{24} + 2HCl$$

may account for the change but present evidence is not conclusive. Molecular weight determinations were reasonably satisfactory but the carbon analysis was low. The latter may be caused by difficulty in obtaining complete combustion because, on burning, the substance leaves a non-oxidizable carbonaceous residue.



I



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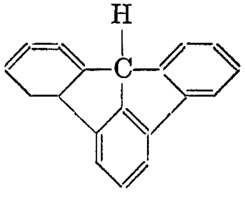

III

This pyrolytic reaction was patterned after the known decomposition (1) of triphenylmethyl chloride, $(C_6H_5)_3CCl$, into II. In view of the conflicting reports in the literature regarding conditions for this pyrolysis, a study of it was undertaken, preceding the experiments mentioned above. The various conditions reported in the literature were duplicated. In addition, runs were carried out in solvents (Halowax and quinoline), or by distilling through a heated Pyrex tube, or by heating triphenylmethyl chloride vapors at 700°; but it never was possible to isolate 9-phenylfluorene in a yield greater than 10%. Yields up to 26% of

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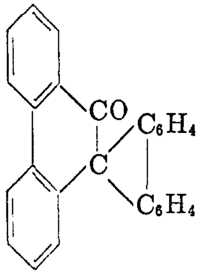
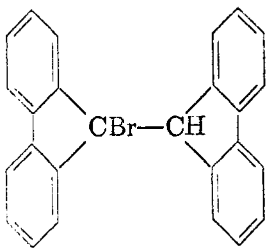
[1] duPont Fellow, 1943–1944. Present address: Parke, Davis and Company, Detroit, Michigan.

triphenylmethane were obtained in some cases. Pyrolysis of triphenylmethyl acetate was tried also. Although acetic acid was evolved, the products consisted of triphenylmethane and higher condensation products, but no 9-phenylfluorene was isolated.

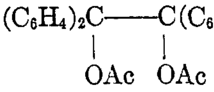
Since the pyrolytic synthesis of III was not satisfactory, a chemical synthesis of I was undertaken, the procedure being patterned after the synthesis of phenanthrene as carried out by Bardhan and Sengupta (2). This involved as the first step the synthesis of ethyl 2-cyclohexanonecarboxylate, by the condensation of cyclohexanone and ethyl oxalate (3). In the next step 9-chlorofluorene was prepared. For this purpose fluorene was first oxidized to fluorenone. Hydrogenation of the latter with nickel gave 61% yields of fluorenol, whereas reduction by sodium and alcohol yielded only a syrup. Fluorenol was converted in nearly quantitative yield into chlorofluorene by interaction with concentrated hydrochloric acid. The corresponding bromide was prepared in good yield also from fluorenol and hydrobromic acid, and in 40% yield by the use of a solution of dry hydrogen bromide in glacial acetic acid (4) at room temperature; but curiously, quite different results were obtained when a solution of hydrogen bromide in hot glacial acetic acid was used. Evidently the temperature at which this reaction is carried out has a considerable influence in determining its course. In the latter reaction the two chief products were 10,10-diphenylenephenanthrone (IV) and a crystalline bromide which seemed to be 9-bromo-9-(9′-fluorenyl)fluorene (V) contaminated with a hydrocarbon, presumably bisdiphenyleneethane or bisdiphenyleneethylene. Some fluorene was isolated also.



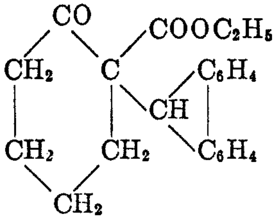
IV



V

Compound IV is known, but V is new. Klinger and Lonnes (5) identified IV as a product from the reaction of bisdiphenyleneethylene acetate,  $(C_6H_4)_2\underset{\text{OAc}}{C}-\underset{\text{OAc}}{C}(C_6H_4)_2$, with 70% sulfuric acid at 100°. This compound is also identical with that isolated by Graebe and Stindt (6) from the hydrolysis of bisdiphenyleneethylene bromide at 150°.

Ethyl 2-fluorenyl-2-cyclohexanonecarboxylate (VI) was synthesized by condensation of 9-chlorofluorene and ethyl potassio-2-cyclohexanonecarboxylate.



VI

Saponification of this ester gave rise to 2-fluorenylcyclohexanone, which was hydrogenated catalytically to 2-fluorenylcyclohexanol. The sodium reduction of this ketone was less satisfactory, much of the ketone being unchanged. Furthermore, the phenylurethans of the alcohols prepared by the two methods melted at different temperatures. Since there are two asymmetric centers in the alcohol, it is possible that one racemic mixture was obtained from the sodium reduction and the other racemic mixture from the catalytic reduction.

Cyclodehydration of 2-fluorenylcyclohexanol to 1,9-cyclohexylenefluorene (I) was accomplished in 60% yield by the use of syrupy phosphoric acid (7). Phosphorus pentoxide (8) gave far smaller yields of crystalline product, the chief substance formed being a syrup which absorbed bromine to give an impure green-black solid. Sulfuric acid was tried also, but difficulties of sulfonation were encountered. Attempts to hydrolyze the sulfonic acids produced were ineffective, although similar hydrolytic experiments carried out with fluorenesulfonic acids did give fluorene in good yield. The 1,9-cyclohexylenefluorene was a colorless solid which melted at 111.5–112°.

As was mentioned earlier, dehydrogenation of I gave rise to 9-phenylfluorene. This was produced in excellent yields by treatment with palladium-charcoal catalyst in a refluxing solution of *p*-cymene, and in lower yields by use of selenium at 280–290°. Since the production of phenylfluorene from I involves an unusual carbon-to-carbon cleavage it becomes necessary to prove that neither cyclohexenylfluorene nor cyclohexylfluorene were produced from 2-fluorenylcyclohexanol by reaction with phosphoric acid. Cyclohexenylfluorene may be dismissed from consideration since the hydrocarbon was inert towards bromine and towards potassium permanganate, pointing to its essentially saturated nature. Cyclohexylfluorene was eliminated since it is known (18) to melt at 102–103°. Furthermore, since the C,H percentages in $C_{19}H_{18}$ and $C_{19}H_{20}$ differ by 0.76, combustion data also are sufficient for a decision. The data were very satisfactory for $C_{19}H_{18}$.

EXPERIMENTAL

All melting points and boiling points are corrected.

Pyrolysis of triphenylmethyl acetate. Pyrolysis of 5 g. of triphenylmethyl acetate (9) in a 5-cc. distilling flask for eighty minutes at 250° and 35–45 mm. yielded 1.0 g. of crude triphenylmethane (isolated by slow evaporation of a benzene solution of the product) and 1.2 g. of an unknown tan solid. The latter crystallized from xylene-butanol in pale yellow crystals (*Anal.:* C, 93.21; H, 5.34) which did not melt below 280°. On burning, the material formed a persistent carbonaceous residue.

9-Chloro-9-phenylfluorene. 9-Phenyl-9-fluorenol was synthesized (10) and from it 9-chloro-9-phenylfluorene, m.p. 78–79°, was prepared by interaction with acetyl chloride.

For this synthesis, 5 g. of the fluorenol was dissolved in 10 g. of acetyl chloride and the mixture was poured into 20 ml. of concentrated hydrochloric acid. The yellow oil which separated soon solidified; m.p. 78–79°. The yield was nearly quantitative.

Pyrolysis. No change in the 9-chloro-9-phenylfluorene was apparent below 250° but at higher temperatures (250–290°) hydrogen chloride was evolved. Heating of 5 g. of it was continued for three hours, after which the cooled material was extracted with hot benzene, from which 4 g. of solid was precipitated by addition of hexane. The solid was insoluble in hot alcohol or ether but was crystallized (pink crystals) from xylene. The crystals did not melt below 280°. On burning, the substance left a non-oxidizable carbonaceous residue. A qualitative test for halogen was negative.

Anal. Calc'd for $C_{38}H_{24}$: C, 94.98; H, 5.02; molec. wt., 480.
Found: C, 91.57; H, 5.63; molec. wt. 468.

9-Fluorenol. Fluorenone (11), 53.6 g., was dissolved in 100 ml. of absolute ethyl alcohol and 5.5 g. of powdered nickel on kieselguhr catalyst (Victor Chemical Co.) was added. A 450-ml. bomb was employed and was charged with 115 atm. of hydrogen. The temperature was maintained at 70–75° and the theoretical amount of hydrogen was absorbed after four hours. A crude yield of 33.9 g. (63%) of fluorenol, m.p. 151–154°, was obtained by crystallization from the solvent. This was purified by recrystallizing from benzene to give 32.8 g. (61%) of product which melted at 153–154° (lit. 156°).

9-Chlorofluorene. An almost quantitative yield was obtained by allowing 33.0 g. of fluorenol to stand with 190 ml. of concentrated hydrochloric acid for twenty-four hours with intermittent shaking. The 9-chlorofluorene was filtered, washed with aqueous alcohol and dried, m.p. 91° (lit. 91°).

9-Bromofluorene. A. A sample of fluorenol (4.14 g.) was allowed to stand with intermittent shaking with 41 ml. of 41% hydrobromic acid for thirty-six hours. At the end of this time, the solid material was filtered off, washed with aqueous ethanol and dried to give 5.02 g., m.p. 99–101°. Several crystallizations from 95% ethanol yielded 3.72 g. (66%) of product, m.p. 104°. The remainder of the material melted over the range 125–130° and was probably a mixture of fluorenol and 9-bromofluorene. Undoubtedly, better yields could be obtained by more careful control of the conditions.

B. A sample of fluorenol (0.32 g.) was dissolved in 10 ml. of glacial acetic acid. Twice the equimolar amount of dry hydrogen bromide, generated by dropping bromine into refluxing tetralin, was passed into a second 10-ml. portion of glacial acetic acid. These two solutions were mixed at room temperature and most of the solvent removed *in vacuo* after the mixture had stood for a few minutes. Crystals formed upon the addition of a small small volume of pentane. A 40% yield (0.17 g.) of 9-bromofluorene, m.p. 103–104°, was obtained in addition to impure fluorenol.

C. Fluorenol (32.78 g.) was dissolved in 250 ml. of glacial acetic acid warmed upon the steam-bath. Dry hydrogen bromide was bubbled into the warm solution for two hours, at which time the solution had become a deep amber color. On cooling, a pale yellow crystalline solid separated which turned brown at 160° and melted at 218°. Recrystallization from benzene gave white crystals which melted at 257–258°. Further crystallizations led to the isolation of 7.5 g. of 10,10-diphenylenephenanthrone (IV), m.p. 256–258°; 11 g. of an impure fraction, turning red at about 190° and melting to a red liquid with the evolution of gas; and 8.5 g. of red-brown syrup of sharp odor. One gram of fluorene, m.p. 114°, was separated from the last by distillation.

The identification of 10,10-diphenylenephenanthrone was accomplished by heating for a short time with alcoholic sodium ethoxide followed by acidification to yield 2-(*o*-fluorenylphenyl)benzoic acid (5), m.p. 240–242° (lit. 242°), neutral equivalent 364 (theoret. 362).

The 11-g. fraction was identified as chiefly 9-bromo-9-(9′-fluorenyl)fluorene (V) by halogen analysis, by reduction, and by treatment with alcoholic potash. The halogen determination was carried out according to the directions of Umhoefer (12). (Calc'd: Br, 19.6. Found: Br, 17.6.) A 0.5-g. sample was refluxed for two hours with 1.0 g. of zinc dust and 25 ml. of benzene. Two fractions of crystals were obtained, one of which was pale yellow and melted at 224–225°, apparently the purified starting material. The other fraction was orange and melted over a range of 160–180°. Recrystallization from 95% ethanol led to a few beautifully formed red crystals, m.p. 173–174°. A molecular weight determination on the material melting at 160–180° indicated a molecular weight of 327. Bisdiphenyleneethylene (5, 6) has the molecular weight 328 and is a red solid, m.p. 189–190°. Contamination with bisdiphenyleneethane would lower the melting point and fade the color but would only change the molecular weight by two units.

Another sample of the 11-g. fraction (0.2 g.) was dissolved in 20 ml. of a 10% ethanolic potassium hydroxide solution, and the mixture was refluxed for three hours. Addition of water to the resulting red solution gave a brick red precipitate melting below 150° and containing no halogen. Upon acidification of the filtrate, a yellow solid precipitated which was purified by crystallization from xylene, m.p. 241.5–242°. This was believed to be bisdiphenyleneethane, lit. m.p. 242, 244° (6, 13, 18).

Ethyl 2-fluorenyl-2-cyclohexanonecarboxylate (VI). The procedure followed was patterned after a similar preparation carried out by Bardhan and Sengupta (2). Ethyl 2-cyclohexanonecarboxylate, b.p. 109° (13 mm.), was prepared in 35% yield by the method of Kotz and Michels (3), starting with cyclohexanone and ethyl oxalate. Potassium (0.90 g., 0.033 mole) was powdered under xylene, the latter replaced by dry benzene and 3.80 g. (0.023 mole) of ethyl 2-cyclohexanonecarboxylate was added. The solution became warm, the potassium melted and a yellow precipitate settled out as the solution turned red in color. A benzene solution of 9-chlorofluorene was added and the volume brought to about 40 ml. with additional benzene. Refluxing was carried out over a period of twenty-four hours, after which the solution was cooled, washed with water, dried with sodium sulfate and the benzene evaporated *in vacuo*. Crystallization was accomplished by dissolving the residue in a small amount of benzene and adding an excess of ligroin. A 35% yield of white crystalline material, m.p. 133.0–133.5°, was obtained. In later preparations it was found that fractional crystallization from glacial acetic acid served well to separate the product from unreacted starting material.

Anal. Calc'd for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63.
Found: C, 79.10; H, 6.64.

Oxime. This derivative was prepared readily by refluxing the keto ester with hydroxylamine hydrochloride in pyridine and ethanol (14a). Purification was accomplished by several crystallizations from 95% ethanol, m.p. 170.5°.

Anal. Calc'd for $C_{22}H_{23}NO_3$: N, 4.01. Found: N, 3.86.

2-Fluorenylcyclohexanone. Five grams of the keto ester (VI) was dissolved in 50 ml. of 95% ethanol containing 5.0 g. of potassium hydroxide. This solution was refluxed on the steam-bath for twenty-two hours. At first a rather vigorous foaming was noted, then the solution became pale yellow in color and some white solid precipitated at the sides. This dissolved upon the addition of 25–30 ml. of water, leaving a few ml. of darker liquid layer at the bottom. The solvents were removed *in vacuo* at room temperature and a white amorphous solid separated. Hydrochloric acid was added to acidity, and the white solid seemed to dissolve with the evolution of considerable gas and the formation of a different, white insoluble compound which gave a yellow oil upon short heating. This mixture was extracted with ether, dried over sodium sulfate, and the ether evaporated to give a viscous amber liquid. Crystallization from aqueous alcohol gave 1.40 g. of white solid, m.p. 112.5–113.5°.

Anal. Calc'd for $C_{19}H_{18}O$: C, 87.00; H, 6.92.
Found: C, 86.99; H, 6.86.

Semicarbazone. The residual syrup was treated with semicarbazide hydrochloride (14b) and 0.89 g. of the semicarbazone, m.p. 220°, was obtained.

Anal. Calc'd for $C_{20}H_{21}N_3O$: N, 13.15. Found: N, 12.77.

The ketone was regenerated by heating for eight hours on the steam-bath with 6 *N* hydrochloric acid. The mixture was filtered, washed with water, dried, and recrystallized from aqueous alcohol to give an 87% yield of silvery-white platelets, m.p. 112.5–113.5°.

2-Fluorenylcyclohexanol. A. Sodium in moist ether was used in an attempt to reduce the above ketone to the corresponding alcohol, but the small amount of product which was obtained could not be purified readily. It apparently contained chiefly the ketone (identified as the semicarbazone) as well as some alcohol, which was indicated by the preparation of its phenylurethan, m.p. 167.5–168.5°.

Anal. Calc'd for $C_{26}H_{25}NO_2$: C, 81.40; H, 6.57.
Found: C, 80.84; H, 6.35.

B. A 1.31-g. (0.0034 mole) sample of the ketone was dissolved in 20 ml. of dioxane (purified by refluxing over hydrochloric acid and distilling from sodium). This solution was placed in a 43-ml. bomb together with 0.5 g. of copper chromium oxide catalyst (15). The bomb was charged with 1330 lbs. of hydrogen and the temperature maintained at 150°. The theoretical amount of hydrogen was absorbed after one and three-quarters hours. The catalyst was removed by centrifuging and the solvent evaporated. The residue was crystallized from 95% ethanol to give 1.11 g. (85%) of beautiful flat stellate clusters of crystals, m.p. 122.0–122.5°.

Anal. Calc'd for $C_{19}H_{20}O$: C, 86.38; H, 7.58.
Found: C, 86.32; H, 7.36.

The phenylurethan of this alcohol was prepared, m.p. 144.5–145.5° (14c). A mixed melting point with the isomeric phenylurethan from the reduction by sodium and moist ether (m.p. 167.5–168.5°) caused a lowering of 20°.

Anal. Calc'd for $C_{26}H_{25}NO_2$: C, 81.40; H, 6.57.
Found: C, 80.93; H, 6.53.

Cyclodehydration of 2-fluorenylcyclohexanol. With phosphorus pentoxide. A 0.1-g. sample of the alcohol (m.p. 120–121°) prepared above by catalytic reduction was heated with 0.2 g. of phosphorus pentoxide in a 10-ml. distilling flask for twenty minutes at 135–140° and 17 mm. of mercury. The temperature was then raised to 170° and maintained for ten minutes (8); the reaction mixture was cooled and water was added with cooling. The mixture was extracted with ether, the extract dried with potassium carbonate, the ether evaporated, and the residue crystallized from alcohol-ether solution by allowing the ether to evaporate. A very small amount of white crystalline material was obtained, m.p. 101–105°, which did not absorb bromine and was unreactive toward potassium permanganate. The major portion of product was an amber syrup which absorbed bromine to give an impure green-black solid.

With concentrated sulfuric acid. To 7 ml. of 90% sulfuric acid was added 0.1 g. of the alcohol over a period of one hour at a temperature of 3–5°. The solution turned a deep rose-violet color, and was removed from the ice-bath and allowed to stand two more hours at room temperature. The solution was then diluted with 60 ml. of ice-water, and a yellow solid precipitated. The physical properties of this solid indicated the presence of a sulfonic acid grouping. Sodium fusion followed by treatment with lead chloride solution gave a black precipitate indicating the presence of sulfur. An attempt to remove the sulfonic acid group by heating with 37% hydrochloric acid in a sealed tube at 200° for twenty-four hours met with failure, although similar treatment sufficed to hydrolyze the sulfonic acid of fluorene in 60% yield.

With syrupy phosphoric acid (7). Twenty ml. of 85% phosphoric acid was distilled up to 230° in a 25-ml. distilling flask. At this point, 0.5 g. of 2-fluorenylcyclohexanol was added and heating continued for one-half hour. The solution was cooled, diluted with water, and extracted several times with benzene. The benzene extract was dried over potassium carbonate, filtered, the filtrate evaporated to dryness, and the residue crystallized from 95% ethanol to yield 0.30 g. of crude product. Further recrystallization led to 0.22 g., m.p. 109–110°, a 44% yield of I. Crystallization by cooling a hot methanol solution of the compound gave beautiful large needles, m.p. 111.5–112.0°. This material did not add bromine and was inert towards alkaline permanganate solution.

Anal. Calc'd for $C_{19}H_{18}$: C, 92.64; H, 7.36.
Found: C, 92.53; H, 7.37.

Dehydrogenation. A. The dehydrogenation of (I) was accomplished by refluxing a solution containing 80 mg. of it in 2 ml. of *p*-cymene with 5% palladium-charcoal catalyst (16). The surface was swept with carbon dioxide during the reaction, and the hydrogen was collected and measured over 50% potassium hydroxide solution. Fresh portions of catalyst were added at intervals to accelerate the reaction. At the conclusion of the reaction the catalyst was filtered off and the filtrate was concentrated by vacuum distillation. Crystallization was induced by the addition of methanol with cooling. An almost quantitative yield of product, m.p. 137–142°, was obtained. Recrystallization from methanol produced fine colorless needles of 9-phenylfluorene, m.p. (and mixed m.p.) 146.5–147°.

Anal. Calc'd for $C_{19}H_{14}$: C, 94.17; H, 5.82.
Found: C, 94.55; H, 5.80.

B. The dehydrogenation of (I) was also accomplished by heating 0.1 g. of the hydrocarbon in a 25-ml. flask with 0.3 g. of selenium at 280–290° for twenty-one hours in a Wood's metal-bath (17); the reaction mixture was cooled and extracted with benzene. After removal of the benzene, the residue was crystallized from aqueous ethanol to give a first crop of 0.03 g., m.p. 137–139°, and a second crop of 0.103 g., m.p. 120–125°. Purification was accomplished by several further crystallizations from aqueous ethanol and a final crystallization from methanol, giving the fine white needles of 9-phenylfluorene, m.p. 142.5–144°.

ACKNOWLEDGMENTS

Micro combustion and micro Dumas analyses were performed by T. S. Ma and Patricia Craig.

SUMMARY

Pyrolysis of triphenylmethyl chloride was carried out under various conditions with no improvement in yield of 9-phenylfluorene over those reported by previous workers. Under similar conditions, pyrolysis of triphenylmethyl acetate yielded triphenylmethane and higher condensation products.

Pyrolysis of 9-chloro-9-phenylfluorene gave rise to good yields of higher dimeric products but no 1,9-*o*-phenylenefluorene.

The synthesis of 1,9-cyclohexylenefluorene was accomplished. Dehydrogenation methods convert this substance into 9-phenylfluorene.

EVANSTON, ILLINOIS

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