Dehydrohalogenation and Hofmann Degradation of the Iodoamine Methiodide XXV.—A suspension of 8.0 g. (0.019 mole) of the methiodide in a solution of 4.3 g. (0.077 mole) of potassium hydroxide and 25 ml. of absolute ethanol was heated under reflux with vigorous stirring for 15 hours. The mixture was filtered and diluted with water. An oily precipitate formed which was insoluble in ether, soluble in water and could be recrystallized from a mixture of absolute ethanol and ether. The identity of this product, of which 1.6 g. was obtained, is still under investigation. The ether extract was dried over magnesium sulfate and removal of ether left a very small residue which was not investigated further. The aqueous solution after ether extraction was evaporated to dryness and the solid was heated to cause decomposition. Water was added to aid in the distillation of the product. Heating followed by addition of water was continued until no further product could be observed. The ether extract of the distillate was dried over magnesium sulfate and evaporation of the ether left a small residue which was distilled under reduced pressure, b.p. about 75° (14 mm.) (reported[7] for the N-methylamine XIII, b.p. 80–81° (15 mm.)). The product was obviously contaminated, being dark in color and having a more pungent odor than that of the N-methylamine XIII. The yield of this crude product was 0.80 g. (36%). A methiodide was prepared, m.p. 254–256°; a mixed melting point with the methiodide of the N-methylamine was not depressed and the infrared spectra of the two samples were identical. A gas chromatograph of the once-distilled amine product showed a large peak at 11.1 min. caused by the N-methylamine and three very small peaks at 9.0, 10.6 and 15.0 min. The chromatograph was run at 149°, with a helium flow of about 60 cc./min. and the retention time of N-methyl-2-aza-1,2-dihydro-*exo*-dicyclopentadiene[7] under these conditions was 9.3 min.

Acknowledgment.—The support of this research by a Research Grant (CY-4298 Cl) of the National Institutes of Health, Public Health Service, and, in part, by a Grant-in-aid of the Allied Chemical Corp. is greatly appreciated.

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

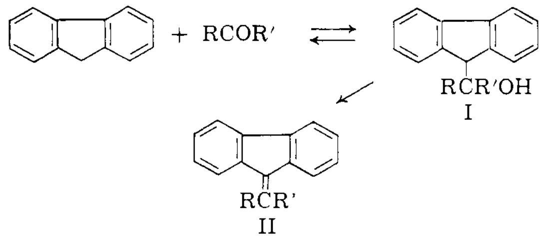
Reactions of Active Methylene Compounds in Pyridine Solution.[1] II. Aldol-type Reactions of Indene and Fluorene[2]

BY EUGENE GHERA AND YAIR SPRINZAK

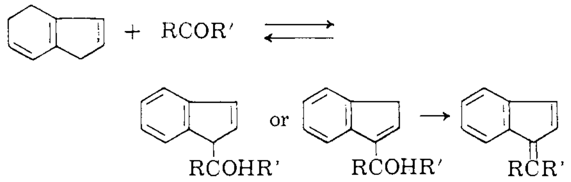
RECEIVED OCTOBER 30, 1959

Indene and fluorene condense with aldehydes in pyridine containing benzyltrimethylammonium hydroxide to give secondary carbinols and the fluorenylcarbinols react further to give β-glycols. Under similar conditions some ketones react reversibly with indene and fluorene to afford tertiary carbinols. Dibenzofulvenes, including alkylidenefluorenes, are ordinarily the major products in the reaction of fluorene with aldehydes at room tempreature. They are also obtainable by dehydration of carbinols, prepared as above, with ethanolic KOH. This dehydration method is also used for the preparation of alkylideneindenes, as the direct preparation from indene and aldehydes has proved unsatisfactory. Under the present conditions two dimers of propylidenefluorene and two trimers of ethylidenefluorene can also be obtained. Structure and mode of formation of these compounds are discussed.

It has long been known that fluorene condenses with aldehydes in the presence of basic catalysts to form dibenzofulvenes (II). While it is generally agreed that reactions of active methylene compounds with carbonyl compounds invariably proceed through an "aldol" stage, no carbinols of structure I have so far been isolated from condensations of fluorene. Carbinols of this type, few of which are known, have been prepared from Grignard derivatives of the hydrocarbon[3] and by other indirect methods.[4] It may further be noted that while the formation of dibenzofulvenes from aromatic aldehydes is relatively easy, difficulties are encountered in the case of aliphatic aldehydes, as these usually undergo self-condensation under the influence of the basic catalyst. No aldol-type reaction of fluorene with ketones has been reported. Similarly, no carbinols of structure III (or IV) have been isolated from the reaction of indene with aldehydes and ketones.



I
II



III IV V

It has now been found that fluorene and indene react readily with aldehydes in pyridine solution and in the presence of benzyltrimethylammonium hydroxide (Triton B). The high reactivity, presumably due to the presence of appreciable concentrations of carbanions under these conditions,[5] allows low enough temperatures to be employed in order to avoid dehydration of the carbinols formed (I and IV, respectively; R' = H), which can thus be isolated in substantial yields. The above hydrocarbons react similarly with certain ketones to give the corresponding tertiary carbinols. Unlike the reaction with aldehydes, the reversible formation of these carbinols is ordinarily uncomplicated by side-reactions (see below).

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(1) Part I, Y. Sprinzak, THIS JOURNAL, **80**, 5449 (1958).

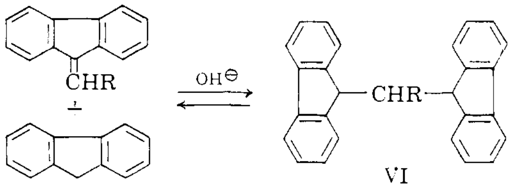
(2) Taken in part from the Ph.D. Thesis submitted to the Hebrew University of Jerusalem by E. Ghera.

(3) C. Courtot, (a) *Ann. chim.*, **4**, 58 (1915); (b) p. 157.

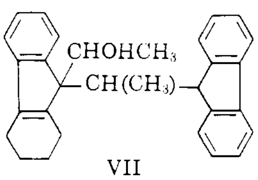
(4) (a) E. J. Greenhow, D. McNeil and E. N. White, *J. Chem. Soc.*, 986 (1952); (b) W. G. Brown and B. Bluestein, THIS JOURNAL, **62**, 3256 (1940); (c) A. Kliegl, F. Weng and G. Wiest, *Ber.*, **63**, 1262 (1930).

(5) See following article, p. 4953.

9-[α-Hydroxyalkyl]-fluorenes.—In the preparation of secondary carbinols (I, R′ = H), the isolation of pure product was easier when fluorene was used in excess, presumably because further reaction of the carbinol with the aldehyde to form a glycol is minimized under these conditions. In some cases the product was accompanied by a considerable amount of a 1,1-bis-[9-fluorenyl]-alkane (VI), apparently resulting from the reversible addition of fluorene to the dibenzofulvene (II) produced by dehydration of part of the carbinol. In one instance—that of acetaldehyde—a small amount of an oxygen-containing by-product was isolated to which structure VII is assigned on the ground of its molecular weight and infrared absorption spectrum.

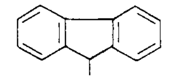


VI



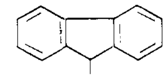
VII

This compound evidently arises from the addition of 9-[α-hydroxyethyl]-fluorene (I, R = Me, R′ = H) to ethylidenefluorene. In contrast with 2-ethylhexanal, which reacted with fluorene at a temperature as low as −30°, the α,β-unsaturated 2-ethylhexenal was recovered unchanged when reaction was attempted below 0°. Reaction took place, however, at room temperature, but rather than the expected carbinol an aldehyde (VIII) was isolated, resulting from a Michael addition of fluorene to the unsaturated aldehyde. In contrast, the expected carbinol IX was isolated from the reaction of fluorene and cinnamaldehyde.



$CH_3CH_2CH_2CHCH(C_2H_5)CHO$

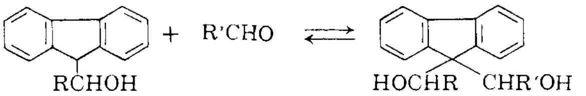
VIII



$C_6H_5CH{=}CHCHOH$

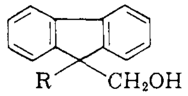
IX

By using an excess of aldehyde, fluorene could be made to react with two molecules of aldehyde to form the hitherto unknown 9,9-bis-[α-hydroxyalkyl]-fluorenes (X). While ordinarily yields were poor, the reaction of fluorene with paraformaldehyde was remarkably easy, affording 9,9-bis-hydroxymethyl-fluorene (X, R = R′ = H), along with a resinous product. The latter possibly results from the polymerization of dibenzofulvene (II, R = R′ = H),[5a] produced by dehydration of the intermediate 9-fluorenylmethanol (I, R = R′ = H).



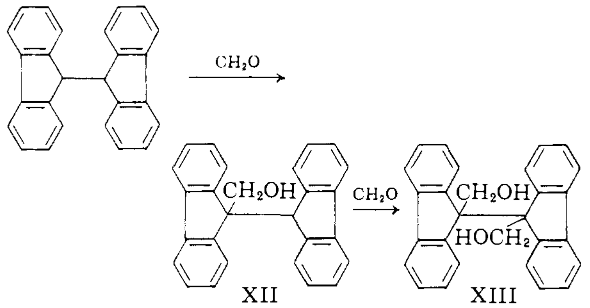
X

A mixed glycol (X, R = H, R′ = Me) was formed when 9-[α-hydroxyethyl]-fluorene (I, R = H, R′ = Me) was treated with paraformaldehyde. Hydroxymethylation also occurred, smoothly, with 9-ethyl-, 9-phenyl- and 9-benzylfluorene, affording carbinols XI (R = Et, Ph and PhCH$_2$, respectively).



XI

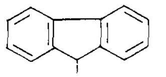
Dibiphenylene-ethane gave, with equal ease, 2,3-dibiphenylene-1-propanol (XII) and 2,3-dibiphenylene-1,4-butanediol (XIII), both of which could be obtained in a good yield by varying the molecular proportions of the reactants.



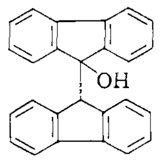
XII XIII

The reversible nature of glycol formation was shown by the observation that oxygen was readily absorbed, with formation of fluorenone,[1] by a solution of 9,9-bis-[α-hydroxyethyl]-fluorene (X, R = R′ = Me) in pyridine containing Triton B. Evidently this reaction is indicative of equilibrium-displacement from glycol to fluorene (through the carbinol), caused by the continual removal of the hydrocarbon.

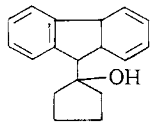
The reaction at low temperature of fluorene with acetone, fluorenone, cyclopentanone and cyclohexanone gave the corresponding tertiary carbinols XIV, XV, XVI and XVII. The reversible nature of these reactions was demonstrated in the first two instances. The carbinol XIV is dissociated into its components at room temperature under identical reaction conditions. In the case of XV, the same equilibrium mixture was obtained at −40° whether the starting compounds were fluorene and fluorenone or their adduct.



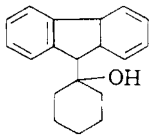
XIV



XV



XVI



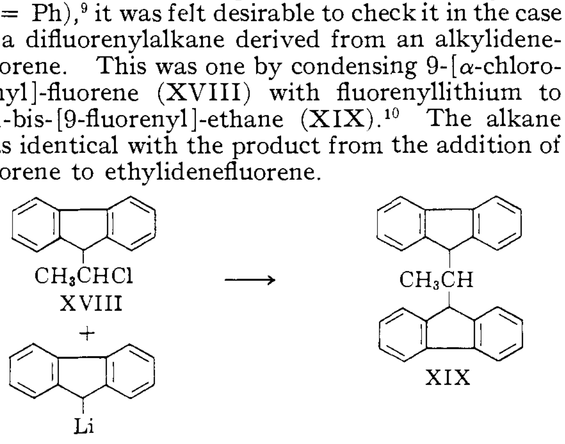
XVII

(5a) H. Wieland, F. Reindel and J. Ferrer, *Ber.*, **55**, 3313 (1922).

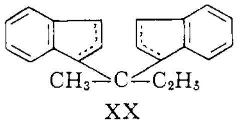
Dibenzofulvenes.—At room temperature, the reaction of aldehydes higher than propionaldehyde with fluorene under the conditions of the present method affords good yields of alkylidenefluorenes (II, R = alkyl, R′ = H). The method is also advantageous for the preparation of the relatively accessible arylidenefluorenes (II, R = aryl, R′ = H), as these are obtained in almost quantitative yields. No alkylidenefluorenes could be isolated from the reaction of formaldehyde and acetaldehyde, undoubtedly because of the instability of the lower alkylidenefluorenes under the conditions of their formation (see below), and propionaldehyde gave but a low yield of propylidenefluorene (II, R = Et, R′ = H). However, alkylidenefluorenes, including the ethylidene and propylidene compounds, can be obtained in good yield by dehydration of the corresponding 9-[α-hydroxyalkyl]-fluorenes with ethanolic potassium hydroxide at room temperature.

1,1-Bis-[9-fluorenyl]-alkanes.—Fluorene is known to add reversibly to dibiphenylene-ethene and to benzalfluorene in pyridine containing saturated aqueous sodium hydroxide to give bisfluorenyl compounds VI.[6] While several compounds of this class have been obtained from fluorene or nitro-fluorenes and aldehydes,[7] there can be little doubt that their formation was due to the same Michael-type addition. The same consideration evidently applies to their formation as important by-products in the condensation of fluorene with aldehydes under the conditions of the present method, as was checked by using fluorene and alkylidenefluorenes as the starting materials.

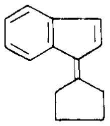
The structure VI assigned to the products of this reaction, in preference to a structure resulting from an inverted mode of addition to the exocyclic double bond in the dibenzofulvene, is that to be expected from the direction of the dipole of this bond.[8] As the structure has been proved in one case only (VI, R = Ph),[9] it was felt desirable to check it in the case of a difluorenylalkane derived from an alkylidenefluorene. This was one by condensing 9-[α-chloroethyl]-fluorene (XVIII) with fluorenyllithium to 1,1-bis-[9-fluorenyl]-ethane (XIX).[10] The alkane was identical with the product from the addition of fluorene to ethylidenefluorene.



3[α-Hydroxyalkyl]-indenes.—These carbinols (IV) were obtained from indene and aldehydes or ketones by procedures similar to those employed in the preparation of carbinols from fluorene. Unlike the latter compounds, the carbinols formed from indene and aldehydes showed no tendency to react with a second molecule of aldehyde. In the reaction with ketones, substantial yields of the carbinols could be obtained at the ordinary temperature; it was thus unnecessary to use lower temperatures, at which, moreover, reaction proved to be very slow. In the condensation with methyl ethyl ketone, the expected carbinol was accompanied by a higher-melting hydrocarbon whose analysis and molecular weight agree with a 2,2-diindenylbutane structure (XX).



XX


XXI

Its formation is analogous to that of difluorenylalkanes. In contrast to fluorene, the reaction of indene with cyclopentanone gave only cyclopentylideneindene (XXI).[11]

The assignment of structure IV to these carbinols follows from the non-identity (as evidenced by their physical properties) of three representative members, *viz.*, 3-[α-hydroxyethyl]-indene (IV, R = Me, R′ = H), 3-[α-hydroxypropyl]-indene (IV, R = Et, R′ = H) and 3-(α-hydroxyisopropyl]-indene (IV, R = R′ = Me), obtained by the present method, with the corresponding 1-isomers (III; replacement as above), prepared from indenylmagnesium bromide.[3a] In the case of the isomeric hydroxyethyl-indenes, the non-identity was further checked *via* the 3,5-dinitrobenzoates. The formation of the 3-isomers under the present (alkaline) conditions is in harmony with Courtot's observation that 1-[α-hydroxyisopropyl]-indene (III, R = R′ = Me), was transformed into the 3-isomer (IV, R = R′ = Me) on treatment with ethanolic potassium hydroxide.[12] Moreover, by using the above alkaline treatment Courtot's 1-[α-hydroxyethyl]-indene (III, R = Me, R′ = H) could be quantitatively isomerized into our carbinol (IV, R = Me, R′ = H).

Benzofulvenes.—The direct preparation of these compounds from indene and aldehydes proved unsatisfactory. The intermediate carbinols formed in this reaction are quite stable at room temperature under the conditions of their formation, and attempts to achieve dehydration by prolonging the reaction time or raising the temperature resulted mainly in the formation of resinous products without substantial increase in the yield of fulvenes. It was found, however, that the latter could be obtained from the carbinols in good yield by heating with ethanolic potassium hydroxide.

Unlike indene, 2,3-diphenylindene gave a good yield of the corresponding fulvene XXII by direct interaction with isobutyraldehyde.

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[6] L. A. Pink and G. E. Hilbert, THIS JOURNAL, **68**, 2014 (1946).

[7] (a) Y. Sprinzak, *ibid.*, **74**, 2116 (1952). (b) G. B. Bachman and S. Polansky, *J. Org. Chem.*, **16**, 1690 (1951).

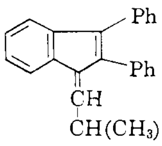
[8] E. D. Bergmann, "Progress in Organic Chemistry," Vol. III, Academic Press Inc., New York, N.Y., and Butterworths Scientfic Publishers, London, 1955, p. 97.

[9] E. D. Bergmann and D. Lavie, THIS JOURNAL, **74**, 3173 (1952).

[10] As fluorenyllithium might be expected to dehydrochlorinate the chloro compound to ethylidenefluorene and further add to this product, it was checked that addition of this kind does not take place under the same conditions, showing that the reaction is one of direct alkylation.

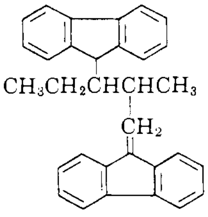
[11] This compound seems to be the first example of a benzofulvene in which the 6-carbon of the fulvene system shares in a cycloalkane ring. Its ultraviolet absorption spectrum, characteristic of a benzofulvene (see Experimental), excludes a cyclopentenyl structure.

[12] C. Courtot, *Compt. rend.*, **160**, 523 (1915).

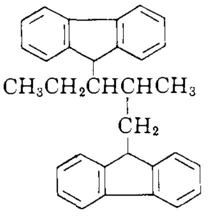


XXII

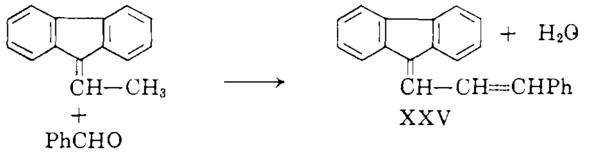
Polymerization of Dibenzofulvenes.—In the course of this work it was observed that the lower 9-[α-hydroxyalkyl]-fluorenes were unstable when kept in pyridine solution at room temperature in the presence of Triton B. Under these conditions, 9-[α-hydroxypropyl]-fluorene (I, R = Et, R′ = H) gave a complex mixture containing propylidenefluorene (II, R = Et, R′ = H), fluorene, 1,1-bis-[9-fluorenyl]-propane (VI, R = Et) and two dimers (*q.v.*) of propylidenefluorene. The presence of the first three compounds is readily accounted for by the ease of dehydration of the carbinol and by the reversible nature of its formation. The last two compounds had almost identical ultraviolet absorption spectra, characteristic of a dibenzofulvene and similar to the spectra of dibenzofulvenes having an additional fluorene nucleus in their molecule.[13] Their infrared spectra showed the presence of an exo-cyclic double bond. We therefore believe that the compounds are the two racemates of structure XXIII, formed from propylidenefluorene by a Michael-type dimerization. The dimerization of propylidenefluorene appears to represent the first instance of a fulvene acting as a donor in a Michael-type addition.[14] The activity of the methylene group adjacent to the exocyclic double bond, as shown in this reaction, falls in line with the observation that ethylidenefluorene condenses readily with benzaldehyde under the same conditions to form cinnamalfluorene (XXV)[15]



XXIII



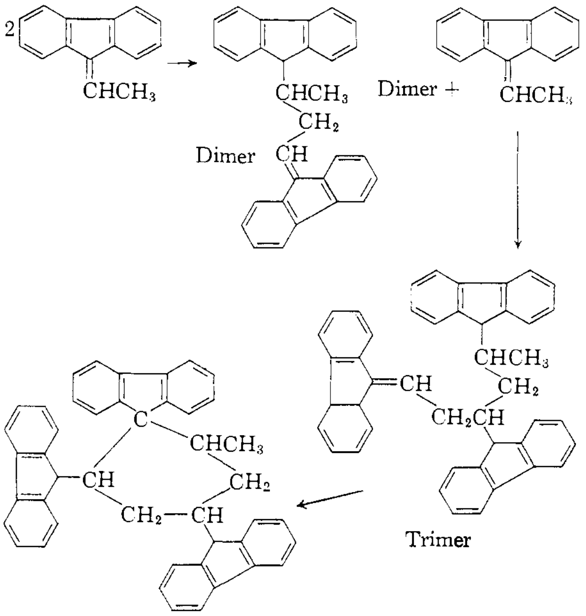
XXIV



XXV

Reduction of the dimers with phosphorus and hydrogen iodide gave products, represented by formula XXIV, with almost identical ultraviolet spectra, similar to those of analogous derivatives of fluorene.[13]

9-[α-Hydroxyethyl]-fluorene also underwent dehydration under similar conditions. While after a short period ethylidenefluorene could be separated from the reaction mixture, prolonged reaction time resulted in the formation of a viscous oil from which two high-melting crystalline hydrocarbons were isolated. These compounds could also be obtained from ethylidenefluorene or from difluorenylethane (XIX). Elementary analysis showed them to be polymers of ethylidenefluorene. The molecular weight of one of them, as determined by X-ray analysis, corresponded to that of a trimer, but the other compound was unadaptable to this method. However, in view of the similarity of their physical properties it is highly probably that the two compounds are isomers. Their infrared spectra did not show the absorption of an exo-cyclic double bond, and their ultraviolet spectra were similar to those of 9-substituted fluorenes.[13] The latter feature seems to exclude acyclic structures for these compounds. Their formation is probably the result of a progressive Michael reaction of ethylidenefluorene, the terminating step consisting of an intramolecular addition. The process may be represented by the scheme



Experimental

Pyridine was dried and a 40% solution of Triton B was prepared as described previously.[1] Indene was distilled before use. Aldehydes and ketones were freshly distilled and titrated for acidity which was usually found to be lower than 7 mole per cent. The petroleum ether used was of b.p. 60–90°.

All reactions performed in pyridine solution were carried out in an atmosphere of nitrogen with stirring. Triton B was not introduced until the flask had been flushed with the inert gas. Acidification of reaction mixtures was by means of acetic acid, diluted with pyridine. Unless otherwise stated, "working up" of a reaction mixture refers to pouring it into a sevenfold volume of water, extracting with ether, washing the ethereal solution successively with water, 10% hydrochloric acid and a sodium bicarbonate solution, and evaporating the solvent after drying.

The identity of known compounds was checked by elementary analysis or by comparison with authentic samples. All melting points are corrected.

Reaction of Fluorene with Aldehydes. 9-Fluorenylmethanol (I, R = H, R′ = H).–Triton B (0.2 ml.) was added to an ice-cold solution of fluorene (11.06 g.) in pyridine (45 ml.) containing suspended paraformaldehyde (2 g.).

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(13) S. Wawzonek and E. Dufek, THIS JOURNAL, **78**, 3530 (1956).

(14) E. D. Bergmann, ref. 8, p. 111.

(15) This reaction has been reported previously by K. Ziegler and F. Crossman, *Ann.*, **511**, 89 (1934), who performed it in ethanolic potassium ethoxide.

After stirring for 3 minutes, the solution was acidified, filtered and poured into water. The solid was filtered, washed and dried. The dry material was heated with alcohol (15 ml.), cooled and the unreacted fluorene (7.4 g.) was filtered off and washed with alcohol (10 ml.). The combined alcohol solutions were evaporated and the residue extracted with boiling benzene (10 ml.). The benzene solution was cooled, filtered and evaporated to dryness. The residue was heated with petroleum ether (7 ml.), and filtration after cooling gave 1.35 g. of the product, m.p. 92–99°. Recrystallization (60% alcohol, Norite) afforded 0.90 g. of the pure carbinol, m.p. 102–103°, lit.[4b] 99.5–100°.

The condensation of fluorene with acetaldehyde, propionaldehyde and butyraldehyde was carried out by the following procedure: a solution of fluorene (16.6 g., 0.10 mole) in pyridine (90 ml.) was cooled to −5°, Triton B (0.4 ml.) was added and the aldehyde (0.05 mole) in an eightfold volume of pyridine was run into the mixture during 50 min. while the temperature was maintained at −5°. After another 10 minutes the reaction mixture was acidified and worked up. The residue from the evaporation of the ethereal solution was boiled with alcohol, left overnight and filtered from fluorene and the corresponding 1,1-bis-[9-fluorenyl]-alkane. The alcohol quantities used for the products from acetaldehyde, propionaldehyde and butyraldehyde were, respectively, 40, 100 and 80 ml. The alcohol extract was evaporated and the residue treated as described below.

9-[α-Hydroxyethyl]-fluorene (I, R = Me, R′ = H).—The residue was dissolved in hot heptane and filtered from carbinol VII (0.2 g.). On standing, a crystalline deposit formed. This was dissolved in cold alcohol, filtered and evaporated. The crystallization of the residue from 60% alcohol gave the carbinol (2.9 g.), m.p. 103–104°, lit.[3b] 102–103°; 3-biphenylene-4-[9-fluorenyl]-2-pentanol (VII), m.p. 260–261° (from benzene).

Anal. Calcd. for $C_{30}H_{26}O$: C, 89.66; H, 6.44; mol.wt., 402. Found: C, 89.70; H, 6.44; mol.wt. (Rast), 388.

9-[α-Hydroxypropyl]-fluorene (I, R = Et, R′ = H).—The residue was crystallized twice from heptane and once from 60% alcohol to afford 4.23 g., m.p. 101–105°. The carbinol was purified by chromatography on alumina in benzene; yield 3.60 g., m.p. 111–111.5° (from heptane).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.92; H, 7.24.

9-[α-Hydroxybutyl]-fluorene (I, R = Pr, R′ = H).—The residue crystallized on treatment with heptane to give 3.1 g. of the carbinol, m.p. 112.5–113.5°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.85; H, 7.50.

9-[α-Hydroxyisobutyl]-fluorene (I, R=*i*-Pr, R′=H).—Fluorene (22.1 g.) and Triton B (0.7 ml.) in pyridine (110 ml.) and benzene (2 ml.) under nitrogen was run during 90 minutes into a solution of isobutyraldehyde (4.8 g.) kept at −22°. Stirring was continued at −22° for 270 min. and the solution was acidified and worked up. The residue was dissolved in boiling alcohol and fluorene removed as before. The alcohol was evaporated and the residue crystallized from petroleum ether; m.p. 83.0–83.5° (5.17 g.).

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.72; H, 7.47.

9-[α-Hydroxy-β-ethylhexyl]-fluorene [I, R=CH(Et)(Bu) R′=H].—Triton B (0.2 ml.) was added to fluorene (5.53 g.) and 2-ethylhexanal (5.0 g.) in pyridine (60 ml.) at −30°, and the mixture was kept at −30° for 75 minutes, acidified and worked up. The residue on distillation gave the carbinol (5.0 g.), b.p. 170–172° (0.4 mm.).

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.42; H, 8.80.

Benzoate, m.p. 92.0–93.8° (from alcohol).

Anal. Calcd. for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59. Found: C, 84.17; H, 7.68.

2-Ethyl-3-[9-fluorenyl]-hexanal (VIII).—Triton B (3 ml.) was added to fluorene (16.6 g.) and 2-ethylhex-2-enal (15.0 g.) in pyridine (160 ml.). The mixture was kept at room temperature for 30 minutes, acidified and worked up. Crystalline fluorene (5.6 g.) was separated from the residue by trituration with cold alcohol and filtration. The crystals were washed with alcohol, and the combined filtrates were distilled *in vacuo*. The aldehyde, (6.3 g.) distilled at 165–169° (0.17 mm.) (on redistillation, b.p. 170–175° (0.30 mm.)). The infrared spectrum showed the characteristic carbonyl absorption and no hydroxyl absorption.[16]

Anal. Calcd. for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 86.38; H, 8.17.

2,4-Dinitrophenylhydrazone.—The aldehyde (2.3 g.), in alcohol, was treated with Brady reagent (70 ml.). The precipitate slowly crystallized; the crystals were dissolved in cold benzene, filtered and evaporated. The residue—yellow crystals—was recrystallized from ethyl acetate, acetic acid and thrice from a 1:1 benzene–heptane mixture; m.p. 183–184°.

Anal. Calcd. for $C_{27}H_{28}O_4N_4$: C, 68.64; H, 5.93; N, 11.86. Found: C, 68.96; H, 6.23; N, 11.60.

Carbinols from aromatic aldehydes were prepared by running the aldehyde (0.05 mole) in pyridine (25 ml.), during 40 minutes, into fluorene (16.6 g., 0.10 mole) and Triton B (0.6 ml.) in pyridine (100 ml.), at −30°. Stirring was continued for another 30 minutes at −30°, and the mixture was acidified and worked up. The residue was worked up as described below.

9-[α-Hydroxybenzyl]-fluorene (I, R=Ph, R′=H).—The residue was extracted thrice with hot petroleum ether (130 ml., 60 ml., 60 ml.) and the combined solution, containing mainly fluorene, was decanted from the deposited crystals after standing overnight. The crude carbinol was recrystallized from alcohol and from heptane to afford 7.2 g., m.p. 121–122°, lit.[4c] 118.5–119°. The alcoholic mother liquor was evaporated and the residue treated with warm heptane, which left undissolved a small quantity (0.3 g.) of glycol X, R = R′ = Ph. The crystals formed after cooling were recrystallized from alcohol to give an additional 1.4 g. of carbinol.

Evaporation of the alcoholic filtrate and washing the residue with warm petroleum ether gave a second portion (0.88 g.) of **9,9-bis-[α-hydroxybenzyl]-fluorene** (X, R=R′=Ph) which, combined with the first portion and recrystallized from benzene–heptane (2:1), afforded 0.76 g. of the pure glycol, m.p. 184–186°.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.71; H, 5.82. Found: C, 85.82; H, 6.00.

A somewhat better yield of glycol (1.6 g.) was obtained when an excess of aldehyde (21.2 g.) was used under similar conditions.

9-[α-Hydroxy-*p*-methoxybenzyl]-fluorene (I, R=*p*-$CH_3OC_6H_4$, R′=H).—Fluorene was removed from the residue by extracting with petroleum ether (2 × 160 ml.). Recrystallization of the carbinol from alcohol afforded 10.8 g., m.p. 122–123°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.45; H, 6.22.

9-[α-Hydroxy-*p*-chlorobenzyl]-fluorene (I, R=*p*-ClC_6H_4, R′=H).—Similar treatment of the residue afforded 7.5 g., m.p. 144.5–145.5° (from alcohol).

Anal. Calcd. for $C_{20}H_{15}OCl$: C, 78.25; H, 4.94; Cl, 11.58. Found: C, 78.11; H, 4.90; Cl, 11.35.

9-[α-Hydroxycinnamyl]-fluorene (IX).—Cinnamaldehyde (4.95 g.) in pyridine (20 ml.) was added during 20 minutes to fluorene (12.45 g.) and Triton B (0.7 ml.) in pyridine (75 ml.) at −30°, and the mixture was acidified after another 10 minutes and worked up. The crude product was washed twice with petroleum ether (70 and 40 ml.), dried *in vacuo* and dissolved in warm alcohol. The cooled solution deposited fluorene (2.25 g.). The carbinol crystallized slowly in the filtrate and was filtered (1.42 g.) after 5 days. Recrystallization (heptane) afforded 0.78 g. of the pure carbinol, m.p. 146–147°. Its infrared spectrum showed hydroxyl absorption and no carbonyl absorption.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.77; H, 5.80.

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[16] The addition of fluorene to the unsaturated aldehyde probably produces two racemates, *cf.*, *e.g.*, E. P. Kohler and T. L. Davis, THIS JOURNAL, **41**, 992 (1919); E. P. Kohler and F. H. Allen, *ibid.*, **46**, 1522 (1924); A. Michael and I. Ross, *ibid.*, **53**, 1150 (1931). Consequently the crude dinitrophenylhydrazone must also consist of a binary mixture, from which only one isomer has been isolated by fractional crystallization.

TABLE I

DIBENZOFULVENES (II, R′ = H)

Aldehyde	R in formula II	Yield, %	B.p. °C.	B.p. Mm.	M.p., °C.	M.p., °C., lit.
Propionaldehyde	Et	12	130–150	0.3	42.5–43.5	44.5–46.0[c]
Butyraldehyde	Pr	55	147–149	.3	54–55	55[d]
Isobutyraldehyde	*i*-Pr	73	130–132	.3	29–30[a]	...
2-Ethylhexanal	(Bu)(Et)CH	85	157–160	.25[b]	.....	...
Benzaldehyde	Ph	95	.....	...	76–77	76[c]
p-Anisaldehyde	*p*-$CH_3OC_6H_4$	97	.....	...	133.5–134.5	128–129[e]
p-Chlorobenzaldehyde	*p*-ClC_6H_4	92	.....	...	151–152	149.5[f]

[a] *Anal.* Calcd. for $C_{17}H_{16}$: C, 92.73; H, 7.27. Found: C, 92.90; H, 7.08. Dibromide, m.p. 129–130° (from petroleum ether), lit. 131–132° (ref. *d*). [b] *Anal.* Calcd. for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.22; H, 8.35. Dibromide, m.p. 108.0–109.5° (from petroleum ether). *Anal.* Calcd. for $C_{21}H_{24}Br_2$: Br, 36.7. Found: Br, 36.8. [c] S. Wawzonek, E. Dufek and N. Sial, *J. Org. Chem.*, **21**, 277 (1956). [d] R. F. Schultz and C. F. Smullin, THIS JOURNAL, **62**, 2904 (1940). [e] Ref. 17. [f] A. Sieglitz, *Ber.*, **52**, 1515 (1919).

By dissolution in ethanolic potassium hydroxide the carbinol was dehydrated to cinnamalfluorene, m.p. and mixed m.p.[17] 157.5–158.5°.

9,9-Bis-hydroxymethylfluorene (X, R = R′ = H).—Triton B (0.2 ml.) was added to fluorene (5.53 g.) in pyridine (45 ml.) containing suspended paraformaldehyde (3.0 g.) at 0°. After stirring at 0° for 40 minutes, the solution was acidified, filtered and worked up using benzene in place of ether. The glycol (2.1 g.), m.p. 145.5–146.5°, crystallized on concentration of the benzene solution.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.70; H, 6.08.

Dibenzoate, m.p. 148–149° (from alcohol).

Anal. Calcd. for $C_{29}H_{22}O_4$: C, 80.17; H, 5.10. Found: C, 80.50; H, 5.02.

9,9-Bis-[α-hydroxyethyl]-fluorene (X, R = R′ = Me). (a) **From Fluorene.**—Fluorene (16.6 g.) and Triton B (0.5 ml.) in pyridine (80 ml.) and benzene (2 ml.) under nitrogen was run during 60 minutes into a solution of acetaldehyde (13.2 g.) in pyridine (60 ml.), at 5–10°. The mixture was left in the ice-bath for 18 hours, acidified and worked up. Distillation gave fluorene, the carbinol (b.p. 130–145° (0.2 mm.) and the glycol (b.p. 145–170° (0.2 mm.). Trituration with petroleum ether containing a little ether, and crystallization from heptane gave 1.1 g. of the pure glycol, m.p. 157–158°.

(b) **From 9-[α-Hydroxyethyl]-fluorene.**—Acetaldehyde (6.5 g.) in pyridine (10 ml.) was run during 15 minutes into a ice-cold solution of the carbinol (2.0 g.) in pyridine (10 ml.) containing Triton B (0.1 ml.). The mixture was kept in the ice-bath for 5 hours, acidified and worked up. The residue crystallized slowly from petroleum ether–ether mixture 4:1. Recrystallization from this solvent afforded 0.25 g. of the glycol, m.p. 157–158°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.52; H, 7.25.

Dibenzoate, m.p. 188.5–189.5° (from alcohol).

Anal. Calcd. for $C_{31}H_{26}O_4$: C, 80.50; H, 5.67. Found: C, 80.60; H, 5.95.

Autoxidation of 9,9-Bis-[α-hydroxyethyl]-fluorene.—The glycol (0.254 g.) and Triton B (0.1 ml.) in pyridine (10 ml.) was stirred in oxygen at room temperature. Absorption of gas (21 ml.) ended in 15 minutes. After working up as usual, the residue was extracted with cold petroleum ether. Fluorenone (0.06 g.), m.p. and mixed m.p. 84–85°, crystallized slowly from the concentrated extract.

9-Hydroxymethyl-9-[α-hydroxyethyl]-fluorene (X, R = H, R′ = Me).—Triton B (0.1 ml.) was added to a solution of 9-[α-hydroxyethyl]-fluorene (1.8 g.) in pyridine (18 ml.) containing supended paraformaldehyde (0.4 g.) at 15°. After 15 minutes, the mixture was acidified and worked up. The residue crystallized from heptane to give 0.47 g. of the glycol, m.p. 124.5–125.5°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.72; H, 6.58.

The mother liquor contained fluorene, unreacted carbinol and ethylidenefluorene.

Reaction of 9-Alkylfluorenes with Formaldehyde.—Triton B (0.15 ml.) was added to a stirred ice-cold mixture of the hydrocarbon (0.025 mole), paraformaldehyde (1.1 g., 0.037 mole) and pyridine (50 ml.); after 30 minutes the mixture was acidified and worked up. The residues gave practically quantitative yields of virtually pure carbinols on seeding with a crystal secured by triturating a drop-sample with water. The solids were recrystallized from petroleum ether.

9-Hydroxymethyl-9-ethylfluorene (XI, R = Et) was obtained in two crystalline forms, m.p. 58.5 and 77.5–78.5°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.94; H, 6.95.

9-Hydroxymethyl-9-benzylfluorene (XI, R = $PhCH_2$), m.p. 100–101°, lit.[18] 98.5–99°.

9-Hydroxymethyl-9-phenylfluorene (XI, R = Ph), m.p. 83.5–84.5°. *Anal.* Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.52; H, 5.73.

Reaction of Dibiphenylene-ethane with Formaldehyde.—Triton B (0.1 ml.) was added to a mixture of the ethane (3.3 g., 0.01 mole), paraformaldehyde (0.90 g., 0.03 mole) and pyridine (60 ml.) and the mixture was acidified after 30 minutes and worked up. The carbinol was extracted from the crude product with boiling 9:1 heptane–benzene mixture; it crystallized from the concentrated solution and by recrystallization (1:2 benzene–heptane) afforded 2.1 g. of **2,3-dibiphenylene-1-propanol (XII),** m.p. 175–176°.

Anal. Calcd. for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.90; H, 5.52.

The insoluble fraction crystallized from a 2:1 benzene–heptane mixture, to give 0.8 g. of **2,3-dibiphenylene-1,4-butanediol (XIII),** m.p. 221.5–222.0°.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 86.50; H, 5.53.

A higher yield (70%) of the glycol, accompanied by the carbinol (in 23% yield), was obtained by using a larger excess (8 moles per mole of hydrocarbon) of formaldehyde. A higher yield (79%) of the carbinol, with only traces of glycol, was secured by using the aldehyde in deficiency (1.5 moles per 2 moles of hydrocarbon). In this experiment the product was separated from the excess ethane by extraction with alcohol.

Dibenzofulvenes (Table I). (a) **From Fluorene and Aldehydes.**—Fulvenes derived from aliphatic aldehydes (propionaldehyde excepted) were prepared by adding Triton B (0.4 ml.) to fluorene (8.3 g., 0.050 mole) and the aldehyde (0.062 mole) in pyridine (80 ml.), at about 25° for 30 minutes, acidifying and working up. The fulvene was isolated by distillation *in vacuo*. The yields given in Table I refer to the recrystallized compounds (from alcohol).

In the case of propylidenefluorene, a lower reaction temperature (15°) and a shorter reaction time (15 minutes) was used.

(b) **By Dehydration of 9-[α-Hydroxyalkyl]-fluorenes.**—The carbinol (1.0 g.) in 0.5–ethanolic potassium hydroxide (10 ml.) was left at room temperature for 24 hours. The fulvene gradually crystallized from the solution. After chilling, the crystals (65–75% yield) were filtered and washed with alcohol. In all cases the melting points showed the products (ethylidene-, propylidene- and butylidenefluorene) to be pure. A trace of red impurity was removed

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[17] J. Thiele and F. Henle, *Ann.*, **347**, 290 (1906).

[18] G. Wittig, P. Davis and G. Koenig, *Ber.*, **84**, 627 (1951).

from ethylidenefluorene by filtration through alumina in petroleum ether solution.

Arylidenefluorenes were prepared by running the aldehyde (0.028 mole), in pyridine (25 ml.), into an ice-cold solution of fluorene (4.15 g., 0.025 mole) and Triton B (0.4 ml.) in pyridine (25 ml.) during 15 minutes. The mixture was left at room temperature for 60 minutes, acidified, poured into water and the precipitated product filtered, washed (diluted HCl, water), dried and recrystallized from heptane.

Reaction of Fluorene with Ketones.—A solution of fluorene (8.3 g., 0.05 mole) and the ketone (0.10 mole) in pyridine (60 ml.) was cooled to −40°, Triton B (0.2 ml.) was added and the mixture was stirred for 6 hours at −40°. In the case of cyclohexanone, additional 0.2-ml. portions were introduced after 2- and 4-hour periods. After acidification, the mixture was poured into water and the precipitated material was filtered after several hours, washed, dried *in vacuo* and treated as described below.

9-[α-Hydroxyisopropyl]-fluorene (XIV).—Fluorene (5.5 g.) was separated from the crude product by boiling with alcohol (40 ml.) and filtering after standing overnight. Two crystallizations (heptane) of the alcohol-soluble residue gave 2.1 g. carbinol, m.p. 102–102.5°, lit.[3b] 99–101°.

1-[9-Fluorenyl]-cyclopentanol (XVI).—The carbinol was extracted from the crude product as above and crystallized from petroleum ether, giving 0.55 g., m.p. 120.5–123.0°. Recrystallization (heptane) raised the melting point to 122.5–123.5°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.45; H, 7.34.

1-[9-Fluorenyl]-cyclohexanol (XVII).—The crude product was boiled with petroleum ether and the crystals were filtered after standing overnight; yield 8.35 g., m.p. 132–134°; after recrystallization from benzene, 134.0–134.5°, lit.[19] 130–131°.

9-Hydroxydibiphenylene-ethane (XV).—Crystallization of the crude product from benzene afforded 14.6 g. of the carbinol, m.p. 197–199°, lit.[20] 195–196°.

Dissociation of XIV at Room Temperature.—The carbinol (1.0 g.) in pyridine (7 ml.) was treated with a drop of Triton B, acidified after 2 hours and poured into water. Fluorene (0.73 g.) was separated by filtration.

Dissociation of XV at −40°.—Triton B (0.15 ml.) was added to the carbinol (2.28 g.) in pyridine (27 ml.) at −40°. After 6 hours, the mixture was acidified and poured into water (200 ml.). The precipitate (1.80 g.) was filtered, washed, dried and heated with petroleum ether. After cooling, the starting material (1.28 g.) was filtered off. The filtrate was chromatographed on alumina to afford 0.27 g. of fluorene and 0.16 g. of fluorenone.

A product of the same composition was obtained in an experiment in which equimolecular quantities of fluorene and fluorenone were used as the starting material under otherwise identical conditions. Only about 7% of XV was formed when the condensation was carried out at room temperature.

1,1-Bis-[9-fluorenyl]-alkanes (Table II). (a) **From Fluorene and Alkylidene-fluorenes.**—The alkanes from butylidene- and isobutylidenefluorene were prepared by adding Triton B (0.1 ml.) to the fulvene (0.005 mole) and fluorene (0.005 mole) in pyridine (20 ml.) at room temperature. After 6 hours, the equilibrium mixture was acidified and worked up. The crude products were crystallized from petroleum ether giving the alkanes in approximately 40% yield.

TABLE II

1,1-BIS-[9-FLUORENYL]-ALKANES (VI)

R in formula IX	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Me	148–149	$C_{28}H_{22}$	93.81	93.60	6.19	6.40
Et	161–163	$C_{29}H_{24}$	93.51	93.40	6.49	6.32
Pr	188–189[a]	$C_{30}H_{26}$	...	...	..	..
i-Pr	228–230	$C_{30}H_{26}$	93.22	93.24	6.78	6.83

[a] Lit. 186–187° (ref. 7a).

Difluorenylpropane was obtained (in 50% yield) by a similar procedure, using a twofold excess of fluorene.

The interaction of fluorene and ethylidenefluorene (in equimolecular quantities) was carried out at 0° for 1 hour; yield 50%.

(b) **From Fluorene and Aldehydes.**—Optimum conditions for this reaction have not been determined. The hydrocarbons were readily separated from the accompanying fluorene in the preparation of 9-[α-hydroxyalkyl]-fluorenes (see above) by crystallization (from heptane) of the alcohol-insoluble material from the extraction of the carbinol. Thus 1.9 g. of the ethane, 3.3 g. of the propane and 5.2 g. of the butane (VI, R = Me, Et and Pr, respectively), were obtained.

Synthesis of 1,1-Bis-[9-fluorenyl]-ethane (XIX).—A mixture of 9-fluorenyllithium[21] (from 1.4 g. of lithium) and 9-[α-chloroethyl]-fluorene[22] (1.0 g.) in dry petroleum ether (30 ml.) was refluxed 18 hours under nitrogen. The excess metal-compound was decomposed with ethanol, water was added and the organic layer separated. Material with b.p. below 207°(4 mm.) was removed and the residue was crystallized from heptane to afford 0.65 g. of the hydrocarbon, m.p. and mixed m.p. 147–148°.

No difluorenylethane was produced when 9-fluorenyllithium was refluxed with ethylidenefluorene under the conditions of the above experiment (see footnote 10).

3-[α-Hydroxyalkyl]-indenes (IV). (a) **From Aldehydes.** (Table III).—The aldehyde in pyridine was run into a cooled solution of indene and Triton B in pyridine. After acidification and working up, the residue was distilled *in vacuo*. The forerun, consisting of a considerable amount of unreacted indene, was followed by an intermediate small fraction of the benzofulvene corresponding to the carbinol product.

(b) **From Acetone and from Cyclohexanone.**—Triton B (0.6 ml.) was added to indene (11.6 g., 0.10 mole) and the ketone (0.20 mole) in pyridine (120 ml.) and the mixture was kept at room temperature for 6 hours, acidified and worked up. The unreacted indene was removed *in vacuo* (b.p. about 80°(25 mm.)) and the residue treated as described below.

3[α-Hydroxyisopropyl]-indene (IV, R = R = Me).—The residue, which solidified on cooling, was crystallized twice (heptane and Norite), to afford 3.52 g. of the carbinol, m.p. 78–79°, lit.[12] 82°.

1-[3-Indenyl]-cyclohexanol.—Crystallization of the oily residue, induced by dilution with petroleum ether and seeding, gave 3.80 g. of the carbinol, m.p. 72–73°; after recrystallization from heptane, m.p. 72.5–73.5°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.45; H, 7.34.

Reaction of Indene with Methyl Ethyl Ketone.—A solution of indene (11.6 g.), the ketone (5.51 g.) and Triton B (0.3 ml.) in pyridine (60 ml.) was left at room temperature for 18 hours, acidified and worked up. **2-[3-Indenyl]-2-butanol (IV, R = Me, R′ = Et)**, was collected on distillation, b.p. 131–133°(4 mm.).

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.75; H, 8.48.

The residue of distillation crystallized on treatment with heptane. The product was decolorized by filtering its benzene solution through active alumina to give 1.05 g. of **2,2-diindenylbutane (XX)**, m.p. 110.5–111.5°.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74; C-methyl, 10.5; mol. wt., 286. Found: C, 91.93; H, 7.72; C-methyl, 9.43; mol. wt. (Rast), 301.

Cyclopentylideneindene (XXI).—The reaction of indene (0.20 mole) with cyclopentanone (0.40 mole) was carried out as described for acetone and cyclohexanone. Distillation of the residue *in vacuo* gave 9.3 g. of a slightly yellow oil, b.p. 121–129°(0.12 mm.), on redistillation 120–124°(0.25 mm.). The product crystallized on treatment with ice-cold alcohol; filtered cold and dried *in vacuo*, it gave colorless crystals of the benzofulvene (5.9 g.), m.p. 43–44°. Recrystallization from alcohol, under nitrogen, gave m.p. 44–45°; ultraviolet absorption λ_{max} (Å.) and log ϵ (in parentheses): 2640 (4.35), 3110 (3.87), 3240 (3.79), 3460–

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(19) J. W. Cock and L. Hunter, *J. Chem. Soc.*, 3168 (1952).

(20) V. Grignard and C. Courtot, *Compt. rend.*, **152**, 1493 (1911).

(21) S. H. Tucker and M. Whalley, *J. Chem. Soc.*, 50 (1949).

(22) Prepared by the procedure used in ref. 13 for 9-chloromethylfluorene.

TABLE III

3-[α-HYDROXYALKYL]-INDENES (IV)

Aldehyde[a]	Indene[b] mole	Reacn. temp., °C.	Time of addn., min.	Total time of reacn. min.	Product (R in formula IV)	Yield, %	B.p. °C.	B.p. Mm.	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Acetaldehyde	0.15	−6	15	90	Me	35	136–138	8	....	$C_{11}H_{12}O$[c]	82.46	82.35	7.55	7.42
Propionaldehyde	.15	0	15	30	Et	42	133–136	5	39.5–40.5	$C_{12}H_{14}O$	82.72	82.70	8.10	8.02
Butyraldehyde	.10	0	45	90	Pr	35	108–109	0.35	41–43	$C_{13}H_{16}O$[d]	82.93	83.20	8.57	8.35
Isobutyraldehyde	.10	0	30	60	*i*-Pr	42	100–102	0.35	....	$C_{13}H_{16}O$[d]	82.93	82.83	8.57	8.50

[a] One-tenth mole, dissolved in a fourfold volume of pyridine. [b] Dissolved in 45 ml. of pyridine. [c] 3,5-Dinitrobenzoate, m.p. 147–149° (from alcohol). *Anal.* Calcd. for $C_{18}H_{14}O_6N_2$: C, 61.06; H, 3.95; N, 7.91. Found: C, 61.09; H, 4.13; N, 8.08. [d] 3,5-Dinitrobenzoate, m.p. 127.5–128.5° (from alcohol). *Anal.* Calcd. for $C_{20}H_{18}O_6N_2$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.90; H, 4.75; N, 7.40.

3470 (3.27); ultraviolet absorption of isopropylideneindene (for comparison)[23]: 2160 (4.41), 3080 (3.80), 3200 (3.72), 3420 (3.22). The compounds deteriorates rapidly in the presence of air.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 91.67; H, 8.01.

Isomerization of 1-[α-Hydroxyethyl]-indene.—The carbinol (III, R=Me, R′=H), m.p. 59°, was prepared according to Courtot.[3a]

3,5-Dinitrobenzoate, m.p. 126–127° (from alcohol); the melting point was depressed on admixture with the 3,5-dinitrobenzoate of the 3-isomer (Table III, footnote *c*).

Anal. Calcd. for $C_{18}H_{14}O_6N_2$: C, 61.06; H, 3.98; N, 7.91. Found: C, 61.03; H, 3.90; N, 8.19.

The carbinol (1 g.) in alcohol (20 ml.) containing potassium hydroxide (0.1 g.) was left at room temperature 60 minutes. Distillation of the product gave an oil, b.p. 136–138°(8–9 mm.), isomeric with the carbinol. The dinitrobenzoate (m.p. 147–149°) was identical with that of 3-[α-hydroxyethyl]-fluorene. The latter carbinol was recovered unchanged under these conditions.

Benzofulvenes (V).—The appropriate carbinol (0.020 mole) in alcohol (60 ml.) containing potassium hydroxide (0.3 g.), was refluxed for 20 minutes, diluted with water, and worked up in the usual manner.

Ethylideneindene (V, R=Me, R′=H), yield 68%, b.p. 109–110°(8 mm.), lit.[3b] 119–121°(17 mm.).

Propylideneindene (V, R=Et, R′=H), yield 65%, b.p. 127–129°(5 mm.), m.p. 26–27° (from alcohol) lit.[3b] b.p. 140°(20 mm.).

Butylideneindene (V, R=Pr, R′=H), yield 62%, b.p. 95°(0.7 mm.). *Anal.* Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.58; H, 8.41.

Isobutylidene-2,3-diphenylindene (XXII).—Triton B (0.25 ml.) was added to an ice-cold solution of 2,3-diphenylindene (1.34 g.) and isobutyraldehyde (0.72 g.) in pyridine (20 ml.) at 0°. After 70 minutes at 0°, the mixture was acidified and worked up. Crystallization from alcohol gave the benzofulvene as yellow crystals (0.95 g., 62%), m.p. 122°, but resolidified above this temperature to melt again at 131–132°. This property was not altered by recrystallization of the melt.

Anal. Calcd. for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.44; H, 6.60.

Dimerization of Propylidenefluorene.—A solution of 9-[α-hydroxypropyl]-fluorene (6.0 g.) and Triton B (0.1 ml.) in pyridine (60 ml.) was kept at 5° for 6 hours, acidified and worked up. The oily product was dissolved in hot heptane (20 ml.) to afford, after prolonged standing, 1.5 g. of crystals of the dimer A, m.p. 161–162°; ultraviolet absorption λ_{max} (Å.) and log ε (in parentheses): 2500 (4.57), 2590 (4.67), 3150 (4.13). The concentrated mother liquor gave, on standing, 0.7 g. of dimer B, m.p. 134.0–134.5° (from heptane), ultraviolet absorption: 2490 (4.45), 2590 (4.58), 3140 (4.06).

Anal. Calcd. for $C_{32}H_{28}$ (Dimer A, XXIII): C, 93.16; H, 6.84; mol. wt., 412. Found: C, 92.90; H, 6.92; mol. wt. (Rast), 385. Found (Dimer B, XXIII): C, 93.25; H, 6.87; mol. wt. (Rast), 408.

From the concentrated mother liquor 1,1-bis-[9-fluorenyl]-propane (0.2 g.) was isolated. The remaining oil contained fluorene and propylidenefluorene.

Reduction of the Dimers of Propylidenefluorene.—A solution of each of the dimers (0.25 g.) in acetic acid (15 ml.) was refluxed for 3 hours with red phosphorus (0.15 g.) and hydriodic acid, sp. gr. 1.65 (2.5 ml.). The filtered solution was poured into water and extracted with benzene. Evaporation and treatment with alcohol induced crystallization of the oily product (0.2 g.).

The two reduced dimers gave mutual depression of m.p.

Reduction product of dimer A (XXIV), m.p. 112–113° (from alcohol); ultraviolet absorption λ_{max} (Å.) and log ε (in parentheses): 2650–2670 (4.50), 2910 (4.02), 3020 (4.19).

Anal. Calcd. for $C_{32}H_{30}$: C, 92.71; H, 7.29. Found: C, 92.45; H, 7.40.

Reduction product of dimer B (XXIV), m.p. 105.5–107.5° (from alcohol); ultraviolet absorption: 2660 (4.52), 2910–2920 (4.02), 3020 (4.16). *Anal.* Found: C, 92.50; H, 7.45.

Trimerization of Ethylidenefluorene. (a).—9-[α-Hydroxyethyl]-fluorene (2.0 g.) and Triton B (0.03 ml.) in pyridine (15 ml.) was kept at 30° for 240 minutes, acidified and poured into water. The precipitated product was filtered off, dried at 60°, treated with boiling heptane and filtered after cooling. After similar treatment with warm ethylene chloride, and crystallization from 1:1 benzene–heptane, trimer A, m.p. 305–308° (0.22 g.), was obtained. The mother liquor, combined with the filtrate from the ethylene chloride treatment, was concentrated to give trimer B, m.p. 297–299° (0.12 g.). The two trimers gave mutual depression of m.p. In another experiment (15.0 g. of 9-[α-hydroxyethyl]-fluorene and 0.7 ml. of Triton B in 150 ml. of pyridine), only trimer A (2.9 g.) could be isolated.

(b).—Ethylidenefluorene (2.05 g.) was kept with Triton B (0.05 ml.) in pyridine (20 ml.) for 210 minutes at 22°. Working up as above afforded 0.22 g. of trimer A and 0.06 g. of trimer B.

(c).—1,1-Bis-[9-fluorenyl]-ethane (2.0 g.), kept with Triton B (0.1 ml.) in pyridine (150 ml.) at 30° for 189 minutes, gave, after treatment with petroleum ether, 0.40 g. of the mixed trimers. Recrystallization as above afforded 0.21 g. of trimer A and 0.03 g. of trimer B. No better separation was achieved by chromatography of the mixture. The petroleum ether extract, chromatographed on active alumina, gave (elution with petroleum ether–benzene 9:1) 0.6 g. of fluorene and (petroleum ether–benzene, 7:3) 0.3 g. of the starting material.

Trimer A, m.p. 305–508°; ultraviolet absorption λ_{max} (Å.) and log ε (in parentheses): 2650–2680 (4.58), 2920–2940 (4.14), 3030–3040 (4.23). *Anal.* Calcd. for $(C_{15}H_{12})_3$: C, 93.75; H, 6.25; mol. wt., 596. Found: C, 93.70; H, 6.20; mol. wt. (X-ray),[24] 590 ± 5%.

Trimer B, m.p. 297–299°; ultraviolet absorption: 2690 (4.62), 2930 (4.18), 3040 (4.21). *Anal.* Found: C, 93.85; H, 6.27.

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[23] A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, Y. Hirshberg and Y. Sprinzak, *Bull. soc. chim. France*, **18**, 702 (1951).

[24] Performed by the Solid State Department of this Institute.