titative hydrogenation it absorbed 0.84 mole of hydrogen per mole of C_7H_9Cl; under the same conditions VIII, prepared by the condensation of cyclopentadiene with vinyl chloride,[6] absorbed 1.05 moles per mole.

It may be concluded that the hydrochlorination product consisted of 80–84% VIII (X = Cl) and 16–20% of VII (X = Cl).

Addition of Hydrogen Bromide to I.—Hydrogen bromide was bubbled into a solution of 8.5 g. (0.09 mole) of I in 26 g. of *n*-pentane at −78° for 10 minutes. The product which contained much excess hydrogen bromide was poured onto ice, washed with dilute alkali and water, dried and distilled. There was obtained 9 g. (56%) of monobromide, b.p. 64–68° (19 mm.), 170–173° (760 mm.),[11] n^{20}_{D} 1.5282–1.5292. Its infrared spectrum indicated that it was a mixture, about one-third of which was 3-bromonortricyclene (VII, X = Br) as shown in comparison with the spectrum of product prepared by the reaction of 2-norbornene with bromine.[5]

3-Nortricyclyl formate (IX) was obtained by the acid-catalyzed reaction of I with formic acid.[14] A mixture of 17 g. (0.18 mole) of I, 76 g. (1.5 moles) of 90% formic acid and 2 g. of boron fluoride etherate was shaken at room temperature for 5 hr. during which the originally two-phase system became a single deep amber solution. The product was treated with water, extracted with ether and the extract was washed, dried and distilled. There was obtained 16 g. (63%) ester, chiefly 3-nortricyclyl formate, b.p. 79° (21 mm.), n^{20}_{D} 1.4758, d^{20}_{4} 1.1103; mol. ref. calcd. for $C_8H_{10}O_2$ (IX) 34.45, obsd. 35.08.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.37; H, 7.52.

The compound absorbed 0.11 mole of hydrogen per mole in the presence of platinum oxide.

The infrared spectrum showed a major intensity band at 12.3 μ indicative of the nortricyclene structure. Minor bands between 14.3 and 15.3 μ showed the possibility of contamination of the sample with a minor amount of a compound containing a double bond in the ring, *e.g.*, 5-norbornen-2-yl formate.

3-Hydroxynortricyclene (X).—Addition of 5 g. of IX to a solution of 4 g. of potassium hydroxide in 10 g. of ethanol resulted in an exothermic reaction accompanied by the precipitation of a small amount of salt. On standing, the mixture separated into two layers, most of the salt going into solution. Water was added and the product was extracted with pentane. Evaporation of the pentane yielded 3 g. (75%) of crystalline compound, m.p. 101–102°, the infrared spectrum of which was similar to that reported for 3-hydroxynortricyclene.[5] Its phenylurethan melted at 143–144°.[5]

2-Norbornyl Formate (XI).—A mixture of 30 g. (0.32 mole) of 2-norbornene, 100 g. (1.9 moles) of 88% formic acid and 2 g. of boron fluoride etherate was heated under reflux (102–103°) for 1 hr., during the first half of which the originally two-phase system became homogeneous. Distillation of the extracted and washed product yielded 32 g. (71%) of XI, b.p. 76–77° (20 mm.), n^{20}_{D} 1.4641; mol. ref. calcd. for $C_8H_{12}O_2$ 36.43, obsd. 36.72.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.59; H, 8.74.

The product absorbed no hydrogen under the usual hydrogenation conditions.

***exo*-Norborneol (XII).**—When 13.5 g. of XI was added to a solution of 11 g. of potassium hydroxide in 30 g. of 95% ethyl alcohol, an exothermic reaction occurred and a white salt separated. The mixture was allowed to stand for an hour and water was then added. The oil which separated soon crystallized. Filtration yielded about 6 g. of crude XII, m.p. 126°.[15] Extraction of the aqueous solution with pentane yielded 2.4 g. (78% total yield) additional product, m.p. 125°. Its phenylurethan melted at 144°.[15]

It is of interest to note that both X and XII yielded phenylurethans melting in the range 143–144°. The melting point of a mixture of approximately equal amounts of the two derivatives was only slightly depressed to 140–140.5°.

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[14] *Cf.* H. B. Knight, R. E. Koos and D. Swern, THIS JOURNAL, **75**, 6212 (1953).

[15] G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

DES PLAINES, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY, JERUSALEM]

1,2-Cyclopentenofluorenes and Some Derivatives of 1,2,3,4-Tetrahydrofluorene

BY ERNST D. BERGMANN AND RAPHAEL IKAN

RECEIVED NOVEMBER 25, 1955

1,2-Cyclopentenofluorene, 3′-methyl-1,2-cyclopentadienofluorene and 3′-methyl-1,2-cyclopentenofluorene have been prepared from fluorene-1-aldehyde, by standard procedures. The spectra of the 1,2-cyclopentenofluorenes are identical with those of a series of hydrocarbons, obtained by Jacobs and co-workers in the dehydrogenation of cevine and jervine. A by-product of the reduction of fluorenone-1- to fluorene-1-carboxylic acid with sodium amalgam has been identified as 1,2,3,4-tetrahydrofluorene-1-carboxylic acid. 1,2,3,4-Tetrahydrofluorene behaves as a true indene derivative in condensing with *p*-chlorobenzaldehyde to a (substituted) benzofulvene.

Craig and Jacobs[1] and Craig, Jacobs and Lavin[2] have obtained by dehydrogenation of cevine (I) a number of polycyclic aromatic hydrocarbons of which the simplest one, $C_{13}H_{12}$, has been identified as the liquid 4,5-benzhydrindene. In addition, a homologous series of hydrocarbons $C_{17}H_{16}$, $C_{18}H_{18}$, $C_{19}H_{20}$ and $C_{24}H_{30}$ (m.p. 160–165°, 116–118°, 185–188°, 108–110°, respectively) has been isolated. They have been assumed to be derivatives of 1,2-cyclopentenofluorene (II) ($C_{16}H_{14}$). Their spectra are very similar and the presence of the fluorene system was indicated by their chemical behavior.[3] The same type of compounds ($C_{20}H_{22}$, $C_{24}H_{30}$) is produced by the dehydrogenation of jervine (III) together with substances ($C_{20}H_{16}$, $C_{22}H_{20}$) believed to be derivatives of 1,2-cyclopenteno-7,8-benzofluorene (IV).[3,4]

It appeared of interest to prepare the unknown 1,2-cyclopentenofluorene (II) and to compare it and its simple alkyl derivatives with the products obtained by the above dehydrogenation reactions.

Fluorenone-1-carboxylic acid (V) was obtained by oxidation of fluoranthene[5,6] and reduced to fluorene-1-carboxylic acid (VI, R = COOH). A by-product observed in this reduction was identi-

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[1] (a) L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, **129**, 79 (1939); (b) **139**, 263 (1941).

[2] L. C. Craig, W. A. Jacobs and G. I. Lavin, *ibid.*, **139**, 277 (1941).

[3] *Cf.* W. A. Jacobs and S. W. Pelletier, *J. Org. Chem.*, **18**, 765 (1953).

[4] W. A. Jacobs, L. C. Craig and G. I. Lavin, *J. Biol. Chem.*, **141**, 51 (1941); *cf.* W. A. Jacobs and Y. Sato, *ibid.*, **181**, 55 (1949).

[5] R. Fittig and F. Gebhard, *Ann.*, **193**, 149 (1878).

[6] L. F. Fieser and A. Seligman, THIS JOURNAL, **57**, 2174 (1935).

fied as 1,2,3,4-tetrahydrofluorene-1-carboxylic acid (*vide infra*). The acid chloride (VI, R = COCl) was reduced to the corresponding aldehyde (VI, R = CHO) by Rosenmund's method. Condensation of the aldehyde with malonic acid gave β-(1-fluorenyl)-acrylic acid (VII), which was reduced catalytically to β-(1-fluorenyl)-propionic acid. The latter was cyclized by means of polyphosphoric acid to 3'-keto-1,2-cyclopentenofluorene (VIII). Its infrared spectrum shows the carbonyl frequency at 1680 cm.$^{-1}$, in accordance with the frequency usual for aryl ketones, but surprisingly low, if compared with the value of 1721 for 1-indanone.[7] By reduction according to the method of Huang-Minlon,[8] VIII was converted into II, which melted at 120°. Reaction of VIII with methylmagnesium iodide, followed by spontaneous dehydration, gave 3'-methyl-1,2-cyclopentadienofluorene (IX). Its catalytic hydrogenation led to 3'-methyl-1,2-cyclopentenofluorene (X), m.p. 121°.

The hydrocarbon $C_{17}H_{16}$ described by Craig and Jacobs[1-2] has m.p. 160–165° and is, therefore, not identical with X. However, it is possible that X is identical with the compound $C_{18}H_{18}$ (m.p. 116–118°) described by the above-named authors; neither the analysis nor the molecular weight determination exclude the possibility that the compound has actually the formula $C_{17}H_{16}$. In any event, the spectra of II and X are practically identical with those reported for Craig and Jacobs' hydrocarbons. The maxima of their compound $C_{24}H_{30}$, *e.g.*, compare with those of II and X as

$C_{24}H_{30}$		X		II		IX	
λmax, mμ	log ε	λmax, mμ	log ε	λmax, mμ	log ε	λmax, mμ	log ε
270	4.40	270	4.30	270	4.62	295	4.18
287	4.20	284	4.16	282	4.46	320	4.38
295	3.85	291	3.78	292	4.10		
300	3.70	303	3.62	303	3.96		
308	3.65	310	3.20	319	2.38		

The spectrum of IX is different, due to the additional conjugation of the cyclopentadieno double bond with the benzene ring of the fluorene system; IX is a hydrocarbon of yellow color.

There can, therefore, be no doubt that the dehydrogenation of cevine (I) and jervine (III) causes a rearrangement of ring A of the steroid-like system. If the quaternary methyl group at C_{10} is eliminated, one could expect X or the isomeric XI ($C_{17}H_{16}$) to be formed. If this methyl group migrates, 1',3'-dimethyl-1,2-cyclopentenofluorene ($C_{18}H_{18}$) would result. The alkyl groups in the higher homologs should then originate from a breakdown of the rings D and E.[9] The survival of larger alkyl groups in the dehydrogenation products of steroids has been observed before,[10] and experiments toward the synthesis of higher homologs of II are now in progress.

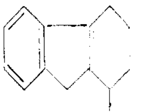
It should, of course, be borne in mind that the identity of the ultraviolet spectra is not a conclusive proof for the identity of the hydrocarbons. Thus, Winkler and Reichstein[11] have pointed out that on the strength of the spectra, the hydrocarbons believed[3,4] to be derivatives of 7,8-cyclopenteno-1,2-benzfluorene may well be alkylated 1,2-benzfluorenes.

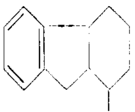
In the reduction of fluorenone- to fluorene-1-carboxylic acid with sodium amalgam an acid of the formula $C_{14}H_{14}O_2$ was obtained as a by-product. As the carbonyl band in its infrared spectrum lies at 1725 cm.$^{-1}$, indicating the presence of a saturated (not aromatic and not α,β-unsaturated) acid,[12] it could be assumed that the compound is 1,2,3,4-tetrahydrofluorene-1-carboxylic acid (XIII). Accordingly, catalytic hydrogenation in the presence of platinum oxide led to the absorption of two hydrogen atoms and the formation of 1,2,3,4,1a,4a-hexahydrofluorene-1-carboxylic acid, probably in the *cis*-form XIV.

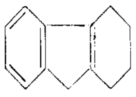
The reduction of benzoic acids to tetrahydro derivatives by means of sodium amalgam is a classical reaction. It is worthy of note that benzoic acid, too, gives the β,γ-unsaturated tetrahydro-acid.[13,14]

Formula XIII is supported by the identity of the ultraviolet absorption spectra of the compound and of 1,2,3,4-tetrahydrofluorene (XV). This spectrum indicates the presence of a double bond conjugated with the aromatic ring, and resembles, therefore, the spectrum of indene[15]: indene, 249 (3.98), 280 (2.70); XV, 260 (4.12), 300 (2.84), 320 (2.70), 336 (2.46); XIII, 261 (4.10).

The hexahydro compound XIV shows the normal benzene spectrum. Compound XV, which is prepared by catalytic cyclodehydration of 2-benzylcyclohexanone,[16] has, indeed, the chemical properties of a substituted indene. It is catalytically reduced to the corresponding indane derivative (1,2,3,4,1a,4a-hexahydrofluorene) and condenses with p-chlorobenzaldehyde to give the beautifully crystallized yellow benzofulvene (XVI). The spectrum of XVI is compared with that of 1-benzylidene-indene[17] and 1-benzylidene-2,3-dimethylindene[18] in Table I.


XIII COOH


XIV COOH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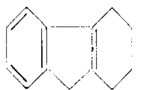
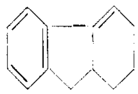

XVI CHC_6H_4Cl


XVII

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[7] E. Bergmann and S. Pinchas, *J. chim. phys.*, **49**, 537 (1952); *cf.* I. Lecomte, *J. Phys. Radium*, **6**, 257 (1945).

[8] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[9] It is recalled that decahydronaphthalene is cracked in the presence of aluminum chloride to methylcyclopentane and polymethylcyclohexanes (G. Chiurdoglu and J. L. Jaminet, *Bull. soc. chim. Belges*, **62**, 4481 (1953); *C. A.*, **49**, 7535 (1955)).

[10] E. Bergmann, THIS JOURNAL, **60**, 2306 (1938).

[11] R. E. Winkler and T. Reichstein, *Helv. Chim. Acta*, **37**, 721 (1954); *cf.* F. Korte, *Ber.*, **88**, 1527 (1955).

[12] L. J. Bellamy, "The Infrared Spectrum of Complex Molecules," Methuen, London, 1954, p. 140.

[13] O. Aschan, *Ann.*, **271**, 231 (1892).

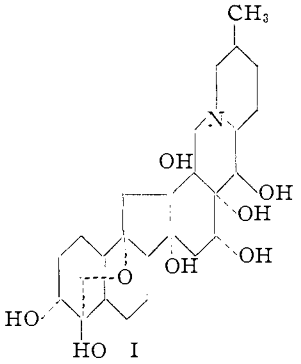
[14] H. Dannenberg and O. Dannenberg-von Dresler (*Ann.*, **593**, 219 (1955)) report that 3,4-aceperinaphthane is reduced by sodium and amyl alcohol to the 1,2,3,9a-tetrahydro derivative.

[15] *Cf.* R. A. Morton and A. J. de Gouveira, *J. Chem. Soc.*, 911 (1934), where more literature is quoted.

[16] J. Colonge and J. Sibeud, *Compt. rend.*, **232**, 845 (1951); *Bull. soc. chim. France*, **20**, 75 (1953).

[17] E. Bergmann and Y. Hirshberg, *ibid.*, **17**, 1091 (1951).

[18] E. Bergmann, *et al.*, *ibid.*, **18**, 669 (1951).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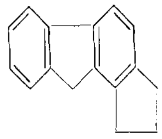
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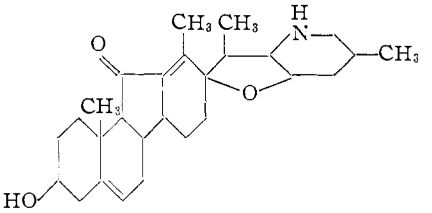
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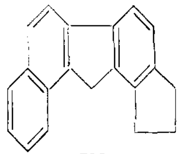
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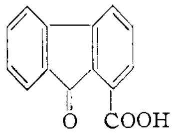
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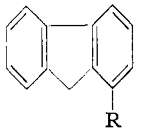
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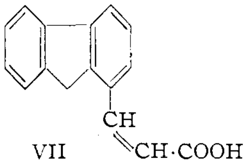
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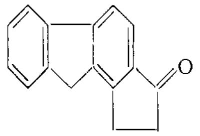
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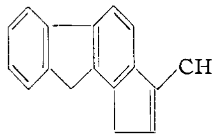
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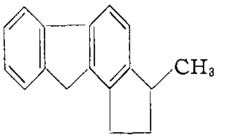
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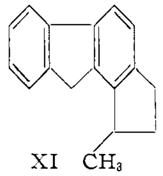
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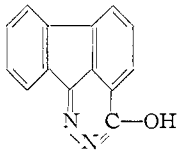
XII

TABLE I

XVI	1-Benzylidene-indene	1-Benzylidene-2,3-dimethylindene
225(4.40)	240(3.98)	256(3.29)
283(4.24)	282(4.10)	
324(4.08)	340(4.54)	320(3.34)

Experimental

Fluorenone-1-carboxylic acid (V) was prepared from fluoranthene according to Fieser and Seligman[6] in a yield of 57%. After recrystallization from ethyl alcohol, it formed orange needles, m.p. 191°. For the reduction to fluorene-1-carboxylic acid, one can either use the method of Fieser and Seligman[6] or that of Bergmann and Orchin.[19] In the former case, a hitherto unknown by-product has been observed.

Fluorene-1-carboxylic Acid (VI, R = COOH) **and 1,2,3,4-Tetrahydrofluorene-1-carboxylic Acid (XIII).**—To 2.5 kg. of 4% sodium amalgam was added 2 l. of ice-water. During 30 minutes, 60 g. of fluorenone-1-carboxylic acid was added to the well-agitated mass. By slow addition of hydrochloric acid, the *p*H of the liquid was kept in the vicinity of the neutral point. The mixture was heated for 4 hours on the steam-bath, cooled, filtered and acidified with 10% sulfuric acid. The colorless precipitate was washed with water, dried and recrystallized from alcohol to give 30 g. of fluorene-1-carboxylic acid, m.p. 245° (lit. 245–246°).

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 80.0; H, 4.8. Found: C, 79.4; H, 4.5.

The alcoholic mother liquor from the preparation of fluorene-1-carboxylic acid was carefully diluted with water and the precipitate dried and recrystallized from benzene; yield 14 g. (from 60 g. of fluorenone-1-carboxylic acid).

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.5; H, 6.5. Found: C, 78.8; H, 6.5.

Methyl Ester.—The acid (3 g.) was methylated at −10° with an ethereal solution of 5 g. of diazomethane. After 12 hours at room temperature, the ether was removed and the residue distilled; b.p. 150° (0.8 mm.), yield 3 g. On standing, the ester solidified; it melted at 42°, d^{27}_4 1.1250, n^{27}_D 1.5652; *MR*, calcd. 65.24 (without exaltation due to conjugation), found 66.12.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 79.0; H, 7.0. Found: C, 79.5; H, 7.1.

An attempt to reduce V to VI (R = COOH) by the method of Huang-Minlon[8] gave the phthalazine XII.[20] The reaction product was precipitated with hydrochloric acid, dried and recrystallized from butyl acetate to give a quantitative yield as colorless needles of m.p. 262°. It contained nitrogen, was refractory to diazomethane, phosphorus pentachloride and thionyl chloride, but dissolved in hot alkali.

Anal. Calcd. for $C_{14}H_8N_2O$: C, 76.4; H, 3.6. Found: C, 76.9; H, 3.9.

The formation of phthalazines from γ-keto-acids under the conditions of the Huang-Minlon reaction is not unusual.[21–24]

Chloride of Fluorene-1-carboxylic Acid (VI, R = COCl). —A mixture of 30 g. of the acid and 180 g. of thionyl chloride was refluxed for 2 hours and the clear, brownish solution evaporated *in vacuo*. The residue was dissolved in benzene and again brought to dryness *in vacuo;* this operation was repeated several times. The crude product melted at 105°; the melting point could be raised by recrystallization from benzene to 108°. The product formed colorless needles; yield 30 g. (83%).

Anal. Calcd. for $C_{14}H_9OCl$: C, 73.7; H, 3.9. Found: C, 73.2; H, 4.1.

Fluorene-1-aldehyde (VI, R = CHO).—With vigorous agitation, a current of pure hydrogen was passed through a boiling solution of 5 g. of the preceding chloride in 50 ml. of dry xylene, containing 0.7 g. of palladium–charcoal (10%) catalyst and 0.1 ml. of the Rosenmund inhibitor. The evolution of hydrogen chloride ceased after 90 minutes. After an additional half-hour of refluxing, the xylene was removed *in vacuo* and the solid residue first distilled (b.p. 158° (0.85 mm.)) and then recrystallized from cyclohexane as colorless needles, m.p. 72°, yield 3.5 g. (83%). The aldehyde has very recently been described by Mulholland and Ward[25]; we have been unable to raise the m.p. of our

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[19] E. Bergmann and M. Orchin, THIS JOURNAL, **71**, 1112 (1949).

[20] For the formulation, see D. J. Drain and D. E. Seymour, *J. Chem. Soc.*, 852 (1955).

[21] E. Bergmann and S. Pinchas, *J. Org. Chem.*, **15**, 1023 (1950).

[22] H. Bowers, T. G. Halsall and G. O. Sayers, *J. Chem. Soc.*, 3070 (1950).

[23] W. G. Overend, L. M. Turton and L. F. Wiggins, *ibid.*, 3500 (1950).

[24] F. L. Weisenborn, D. C. Resny and Th. L. Jacobs, THIS JOURNAL, **76**, 552 (1954).

[25] T. P. C. Mulholland and G. Ward, *J. Chem. Soc.*, 4676 (1954).

aldehyde preparation to 90°, as indicated by the British authors.

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.6; H, 5.2. Found: C, 87.0; H, 5.5.

The dinitrophenylhydrazone formed orange-red needles, after recrystallization from nitroethane, m.p. 262° (Mulholland and Ward[25] report m.p. 284–286° from nitrobenzene).

Anal. Calcd. for $C_{20}H_{14}N_4O_4$: C, 64.2; H, 3.7. Found: C, 64.1; H, 3.8.

β-(1-Fluorenyl)-acrylic Acid (VII).—A mixture of 3 g. of fluorene-1-aldehyde, 1.6 g. of malonic acid, 1.2 g. of pyridine and 3 drops of piperidine was heated for 4 hours at the steam-bath and for 5 minutes at 150°. It was then poured into a mixture of 100 ml. of water and 5 ml. of concentrated hydrochloric acid. The acid was filtered, washed with water, dried and recrystallized from glacial acetic acid as long, colorless needles of m.p. 254°, yield 3.5 g. (97%).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.4; H, 5.1. Found: C, 81.9; H, 5.2.

β-(1-Fluorenyl)-propionic Acid.—A suspension of 3 g. of the unsaturated acid in 150 ml. of dioxane was hydrogenated in the presence of 100 mg. of platinum oxide at elevated temperature and at a pressure of 3 atmospheres. The clear solution of the reduction product was evaporated and the residue recrystallized from glacial acetic acid; colorless needles of m.p. 205°, yield quantitative.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found: C, 80.2; H, 5.8.

3′-Keto-1,2-cyclopentenofluorene (VIII).—With vigorous stirring, a mixture of 2 g. of the preceding acid and 60 g. of polyphosphoric acid[26] was heated at 120–130° for 2 hours. The red product was poured into 200 ml. of cold water and isolated by extraction with ether. The ethereal solution was washed with 10% sodium carbonate solution (from which none of the original acid could be recovered), dried and evaporated. The solid residue was recrystallized from isopropyl alcohol and formed yellowish needles, m.p. 185°, yield 1.2 g. (88%). The infrared spectrum was measured in chloroform (20 mg. in 0.5 ml.).

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.3; H, 5.5. Found: C, 87.3; H, 5.5.

1,2-Cyclopentenofluorene (II).—By the method of Huang-Minlon,[8] 1.3 g. of the preceding ketone was reduced with 1.4 g. of potassium hydroxide, 2 ml. of 85% hydrazine hydrate and 10 ml. of ethylene glycol. The solution was diluted with 15 ml. of water and acidified with 4 ml. of 6 *N* hydrochloric acid. It was extracted once with chloroform and distilled *in vacuo*, b.p. 155° (0.25 mm.). The solid distillate was recrystallized from ethanol as white leaflets, m.p. 120°, yield 1.1 g. (92%).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.2; H, 6.8. Found: C, 93.1; H, 6.7.

3′-Methyl-1,2-cyclopentadienofluorene (IX).—To the Grignard solution, prepared from 0.6 g. of magnesium and 3.3 g. of methyl iodide, 1.7 g. of solid 3′-keto-1,2-cyclopentenofluorene was added. Then the ether was removed and replaced by benzene and the mixture refluxed for 4 hours and after 12 hours at room temperature was decomposed with ice and sulfuric acid. The benzene layer was washed with dilute sodium hydroxide solution and water, dried and evaporated. From glacial acetic acid, yellow crystals, m.p. 197°, were obtained in quantitative yield.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.6; H, 6.4. Found: C, 93.7; H, 6.4.

3′-Methyl-1,2-cyclopentenofluorene (X).—The catalytic hydrogenation of 1 g. of the unsaturated hydrocarbon in 100 ml. of anhydrous alcohol was carried out in the presence of 100 mg. of platinum oxide, at elevated temperature and at 2 atmospheres pressure. From the filtered solution, the product was obtained in quantitative yield, upon evaporation. From glacial acetic acid, colorless crystals of m.p. 121° were obtained.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 93.1; H, 7.3.

1,2,3,4,1a,4a-Hexahydrofluorene-1-carboxylic Acid (XIV).—A solution of 2 g. of the acid XIII in 100 ml. of anhydrous alcohol was hydrogenated at slightly elevated temperature and pressure in the presence of 100 mg. of platinum oxide. When the calculated amount of hydrogen had been absorbed, the solution was filtered and evaporated and the residue recrystallized from cyclohexane, m.p. 138–139°; ultraviolet spectrum: 260 mμ (2.60), 266 mμ (3.55), 272.5 mμ (3.80).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.8; H, 7.4. Found: C, 78.0; H, 7.8.

1,2,3,4-Tetrahydrofluorene (XV).—According to Colonge and Sibeud,[16] 2-benzylcyclohexanone was prepared from cyclohexanone and benzyl chloride by means of sodamide,[27] or by catalytic reduction[27] of 2-benzylidenecyclohexanone[27,28] (b.p. 164–166° (4 mm.), m.p. 53–54°). The cyclodehydration in the presence of aluminum chloride[16] gave an average yield of 40% of XV, b.p. 135–140° (6 mm.), together with a considerable amount of resinous material; $d^{27.5}{}_4$ 1.0189, $n^{27.5}{}_D$ 1.5600; *MR* calcd. 53.76 (without exaltation), found 54.02. Upon standing, the product crystallized partly. The solid crystallized from methanol in form of silvery leaflets, m.p. 57°; ultraviolet spectrum in alcohol: 260 mμ (4.12), (300 mμ (2.84)), 320 mμ (2.70), 336 mμ (2.46).

Anal. Calcd. for $C_{13}H_{14}$: C, 91.8; H, 8.2. Found: C, 91.7; H, 8.6.

In the preparation of XV, a liquid by-product was obtained which upon redistillation showed a constant b.p. of 82–84° (0.4 mm.), which is somewhat lower than that of XV. The fraction could not be induced to crystallize. Its analysis, molecular refraction and ultraviolet spectrum pointed to the formula of a tetrahydrofluorene, in which the olefinic double bond is conjugated to the benzene ring. It has not been decided whether this compound is impure XV or an isomer, such as, *e.g.*, XVII; $d^{25}{}_4$ 1.0035, $n^{25}{}_D$ 1.5533; *MR* calcd. 54.39, found 54.10; ultraviolet spectrum (in alcohol): 252 mμ (3.34) accompanied by some minor bands, 320 mμ (2.56), 335 mμ (1.87).

Anal. Calcd. for $C_{13}H_{14}$: C, 91.8; H, 8.2. Found: C, 91.8; H, 8.0.

9-(*p*-Chlorobenzylidene)-1,2,3,4-tetrahydrofluorene (XVI).—A mixture of 8 g. of XV, 7 g. of *p*-chlorobenzaldehyde, 1 g. of piperidine and 1 g. of finely ground potassium hydroxide was heated azeotropically in 50 ml. of xylene, until no more water appeared in the trap. The xylene solution was then washed with dilute acid, sodium bicarbonate solution and water and dried, and the oily xylene residue distilled *in vacuo*. After some starting material, an orange-yellow oil distilled at 210–215° (0.09 mm.). It crystallized upon trituration with a mixture of methanol and isopropyl alcohol. From isopropyl alcohol beautiful lemon-yellow prisms, m.p. 114–115°, yield 4.3 g., were obtained.

Anal. Calcd. for $C_{20}H_{17}Cl$: C, 82.2; H, 5.8. Found: C, 82.3; H, 6.0.

1,2,3,4,1a,4a-Hexahydrofluorene.—The solution of 1.65 g. of XV in 100 ml. of alcohol absorbed quickly the calculated amount of hydrogen in the presence of 100 mg. of platinum oxide. The product was a colorless oil of b.p. 98° (0.8 mm.), $n^{26}{}_D$ 1.5409 (literature[29] b.p. 107° (15 mm.), $n^{10.9}{}_D$ 1.5572).

Anal. Calcd. for $C_{13}H_{16}$: C, 90.7; H, 9.3. Found: C, 90.2, 90.5; H, 9.2, 9.5.

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