The resonance energy of the allyl radical is about 35% that of the allyl cation.[20] The decreased ability of an α-vinyl group to stabilize a radical compared to a cation is due to electron repulsion arising from the presence of an additional electron in the molecular orbital.[21] Furthermore, it has been calculated that a β-vinyl group is roughly 40% as effective at stabilizing a cation than is an α-vinyl group.[22] Apparently the added electron repulsion in the radical simply outweighs what little stabilization might result from delocalization in a non-classical structure. It is also possible that the different properties of norbornyl and dehydronorbornyl cations and radicals are due to differences in hybridization about a cationic carbon atom and a radical carbon atom. Alternatively, the difference in the cation and radical might be explained by considering C_2, C_5 and C_6 to define a homoaromatic structure[23] in which one carbon atom, C_1, intervenes between C_2 and C_6, and two carbon atoms, C_3 and C_4, intervene between C_2 and C_5. In such a case, the cation, having two electrons in the homoaromatic system, would be expected to be more stable than the radical with its three electrons. Whatever the reason, the formation of non-classical structures is not observed during the rate-determining or product-determining stages of reactions proceeding by way of free radicals at C_2 of a norbornane or norbornene ring system.

Acknowledgment.—It is a pleasure to express our appreciation to the Research Corporation for a Frederick Gardner Cottrell Grant which supported some of the earlier stages of this work, to the Dow Chemical Co. for a fellowship awarded to Mr. De Jongh during the academic year 1961–1962, and to the National Science Foundation for fellowships awarded to Mr. De Jongh during the academic year 1960–1961 and from July, 1962, until the completion of his work.

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[20] A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 1052 (1960).

[21] A. Streitwieser, Jr., *ibid.*, **82**, 4123 (1960).

[22] M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

[23] S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

1,2-Dihydrocyclopent[jk]fluorene

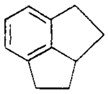
BY BERMA L. MCDOWELL,[1] GERALD SMOLINSKY[2] AND HENRY RAPOPORT

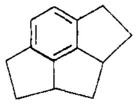
RECEIVED MARCH 28, 1962

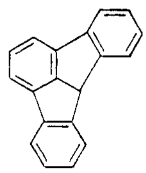
In order to obtain further data on the effects of bending a benzene ring, the strained hydrocarbon 1,2-dihydrocyclopent[jk]fluorene (IV) has been prepared and some of its properties have been determined. Synthesis by pyrolysis of the lead salt of 1-carboxyfluorene-9-acetic acid (V) was unsuccessful. However, by approaching the synthesis through a substituted indan and forming the fluorene by decomposition of diazotized *o*-(1-indanyl)-aniline (XXIX), the cyclopent[jk]fluorene ring system was prepared. As was the case with the previous three compounds of this series,[3] IV displayed properties characteristic of a bent benzene ring—a distinct bathochromic shift with decreased extinction coefficient in its ultraviolet absorption and olefinic-like reactivity with hydrogen and perbenzoic acid.

Introduction.—The objective of a series of investigations[3] has been to synthesize strained aromatic hydrocarbons in which the central benzene ring is forced out of planarity by a fused cyclopentano system. The diminished resonance stabilization, brought about by decreased overlap of the π-orbitals in a warped system, should be evidenced in increased susceptibility of that benzene ring to oxidation and reduction and in other behavior tending toward that of "cyclohexatriene." The ultraviolet absorption bands of such a molecule are expected to show a bathochromic shift and a decreased extinction coefficient when compared with those of a similarly substituted but non-strained planar system. The energy of the excited states of the two compounds would be comparable, but the ground state energy of the strained compound would be higher, thus resulting in a lower energy of transition. There would also be less fine structure in the spectrum of the strained molecule, probably as a result of the increased complexity of vibrational transitions.[4]

These predictions have been confirmed in several strained aromatic hydrocarbons of the above type which have been synthesized: 2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (I),[3a] 2,2a,3,3a,4,5-hexahydro - 1H - cyclopent[jkl] - *as* - indacene (II)[3b] and fluoradene (III).[3c] All three compounds are easily hydrogenated over a palladium-on-carbon catalyst, II and III are readily attacked by perbenzoic acid, and all three show the expected spectral properties (see Table III).


I


II


III

1,2 - Dihydrocyclopent[jk]fluorene (IV) should represent a strained system intermediate between I and III. It is the preparation and properties of this substance that are the subject of this report.

Synthesis.—We anticipated that pyrolysis of the lead salt of 1-carboxyfluorene-9-acetic acid (V)

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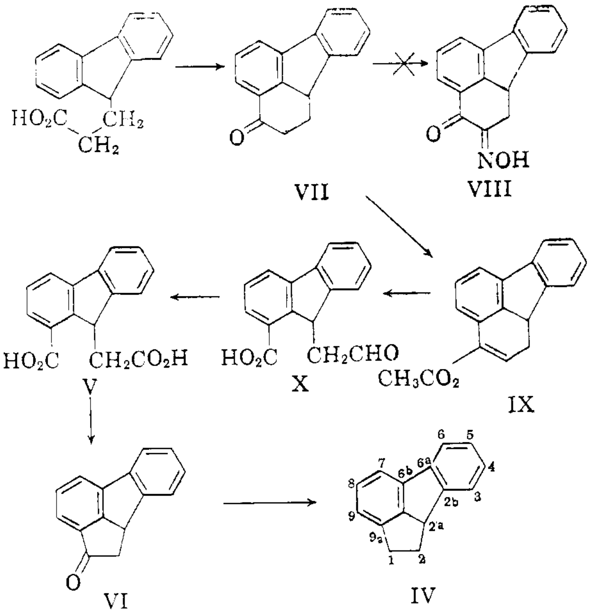
[1] National Institutes of Health Predoctoral Fellow.

[2] National Science Foundation Predoctoral Fellow.

[3] (a) H. Rapoport and J. Z. Pasky, *J. Am. Chem. Soc.*, **78**, 3788 (1956); (b) H. Rapoport and G. Smolinsky, *ibid.*, **82**, 1171 (1960); (c) H. Rapoport and G. Smolinsky, *ibid.*, **82**, 934 (1960).

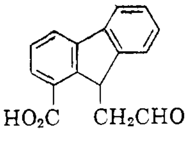
[4] See L. L. Ingraham in M. S. Newman "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 500, and other references on strain in aromatic systems given in footnote 3b.

would yield 1-oxo-1,2-dihydrocyclopent[jk]fluorene (VI) which could be converted to IV by Wolff–Kishner reduction. Both I and II had been prepared in this manner,[3a,b] and the preparation of IV was expected to proceed similarly. Accordingly, the synthesis outlined below was undertaken.

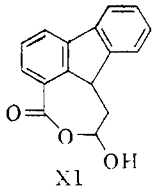


Fluorene-9-propionic acid[5] was cyclized to 3-oxo-1,2,3,10b-tetrahydrofluoranthene (VII) in 85% yield[6] by extending the reaction time in hydrogen fluoride to forty hours. Attempted conversion of VII to 2-oximino-3-oxo-1,2,3,10b-tetrahydrofluoranthene (VIII) resulted in polymeric and highly colored material, probably because the acidic nature of the 10b-hydrogen leads to aromatization of VIII or nitrosation at this position. The enol acetate IX was prepared readily, however, using isopropenyl acetate, and treatment with ozone gave 1-carboxyfluorene-9-acetaldehyde (X). When the aldehyde X was oxidized with hydrogen peroxide in glacial acetic acid and the crude product was crystallized from aqueous ethanol, a poor yield of a difficultly purified diacid V was obtained. This difficulty was traced to the presence of ester which could have arisen from an intermediate anhydride XII. If the aldehydo-acid X is in equilibrium with the lactol XI, oxidation might be expected to give some anhydride XII. Indeed, treatment of the crude oxidation product with ethanol gave material which contained 0.43 ethoxyl radical per molecule. When the isolation procedure included heating with alkali, this ester impurity was eliminated.

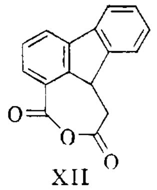
Although diacid V prepared in this manner appeared to be pure, the lead salt prepared from it under a variety of conditions did not give the correct analysis. Several pyrolyses of this lead salt failed to give any indication of the formation of ketone VI. Since the purity of the lead salt has been shown to be a very important factor in the yield of ring-closed ketone from the pyrolysis,[3a] an alternate synthesis of diacid V was devised.



X

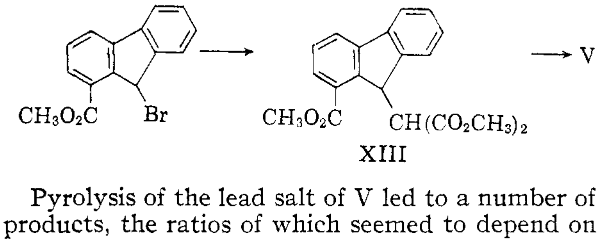


XI

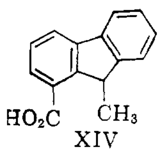


XII

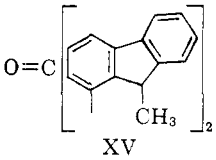
Methyl 9-bromofluorene-1-carboxylate[7] was converted to dimethyl 1-methoxycarbonylfluorene-9-malonate (XIII) via a malonic ester condensation, and hydrolysis and decarboxylation gave pure diacid V in excellent yield. Lead salt prepared from this diacid gave the correct analysis.



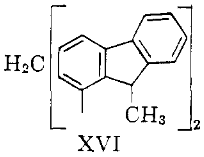
Pyrolysis of the lead salt of V led to a number of products, the ratios of which seemed to depend on the temperature of the pyrolysis. The ultraviolet absorption of the desired ketone VI should resemble that of 1-acetylfluorene,[8] and no such absorption was seen in the spectra of the various fractions isolated by chromatography on alumina of the pyrolysate. Three pure compounds were isolated and were identified as fluorenone, 9-methylfluorene-1-carboxylic acid (XIV) and di-1-(9-methylfluorenyl) ketone (XV).



XIV



XV



XVI

Structure XIV, 9-methylfluorene-1-carboxylic acid, was assigned to the pyrolysis acid on the basis of its analysis and spectral properties. Its ultraviolet absorption was almost identical to that of 1-carboxyfluorene-9-acetic acid (V), showing the hypsochromic shift with alkali characteristic of aromatic acids. The presence of a methyl group on C_9 was established by comparing the nuclear magnetic resonance spectrum of the pyrolysis acid chloride with that of 1,9-dimethylfluorene. The latter showed absorption at 7.65 τ (singlet, C_1–CH_3), 8.63 τ (doublet, C_9–CH_3) and 6.31 τ (quartet, C_9–H). In the pyrolysis acid, the singlet at 7.65 τ was absent and there was a doublet at 8.60 τ (C_9–CH_3) and a quartet at 5.64 τ (C_9–H).

Structure XV initially was postulated for the pyrolysis ketone since it originated in the same reaction as the pyrolysis acid XIV. This structure was confirmed by isolation of the same ketone

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(5) S. H. Tucker, *J. Chem. Soc.*, 803 (1952).

(6) This cyclization has been effected in (a) 77% yield from the acid chloride using aluminum chloride [M. C. Kloetzel and F. L. Chubb, *J. Am. Chem. Soc.*, **72**, 150 (1950)] and in (b) 44% yield from the acid chloride and stannic chloride [A. Campbell and S. H. Tucker, *J. Chem. Soc.*, 2623 (1949)]. The latter reports a 22% yield using hydrogen fluoride.

(7) J. Forrest and S. H. Tucker, *J. Chem. Soc.*, 1137 (1948).

(8) E. D. Bergmann and R. Ikan, *J. Am. Chem. Soc.*, **80**, 5803 (1958).

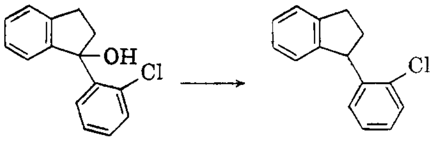
in 24% yield from pyrolysis of the lead salt of XIV. On reduction, this ketone gave the difluorenylmethane XVI, whose ultraviolet absorption was very similar to that of 1,9-dimethylfluorene.

To aid in the identification of other products formed in quite low yield in the pyrolysis of diacid V, the same reaction was carried out with radioactive diacid prepared from dimethyl [α-^{14}C]-malonate. No additional compounds could be identified, but further support for the assigned structures was found in that the radioactive ketone XV had twice the specific activity of the diacid V.

The failure to form the cyclopent ketone VI in the pyrolysis of diacid V is surprising in view of the fact that the cyclopent ketone precursor containing the highly strained ring system present in II was successfully prepared by such a pyrolysis. Perhaps the greater planar rigidity of the fluorene nucleus, as compared to that of the cyclopentindene ring system I, allowed decarboxylation and other decomposition to occur in preference to ring closure.

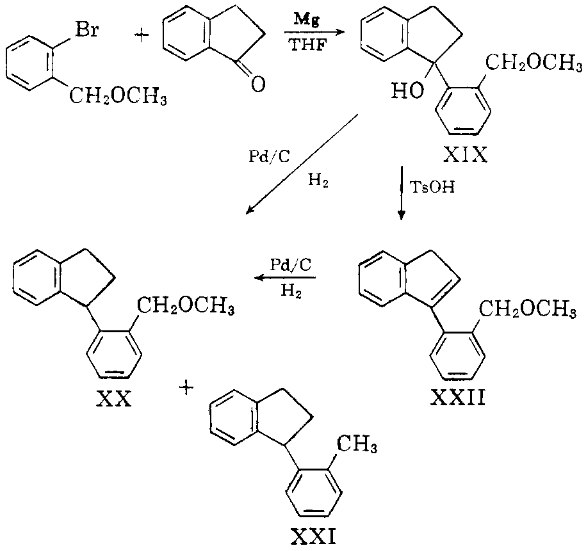
An alternate procedure was suggested by the method which had been used to prepare fluoradene (III).[3c] In this method, the final five-membered ring was formed by joining two aromatic nuclei with elimination of nitrogen from a diazonium salt. As applied to the synthesis of the cyclopent[jk]fluorene ring system (IV), this approach would require a suitably substituted 1-phenylindan and the fluorene nucleus would be formed in the ring-closure step.

Proceeding in direct analogy with the synthesis of fluoradene (III), 1-indanone was treated with the Grignard reagent from *o*-chlorobromobenzene. The intermediate carbinol was reduced with zinc and acid, giving 1-(2-chlorophenyl)-indan (XVII). However, all attempts to replace the chlorine of XVII by cyanide or prepare its Grignard reagent for subsequent carbonation led only to polymeric material. To overcome this impasse, an intermediate was sought in which there was already present a carbon function easily convertible to a carboxyl group, instead of the chlorine.



XVII

This was attained by using the Grignard reagent from 1-bromo-2-methoxymethylbenzene.[9] In tetrahydrofuran, this reagent and 1-indanone gave 1-(2-methoxymethylphenyl)-1-indanol (XIX) accompanied by 2-(1-indanylidene)-1-indanone (XVIII), arising from self-condensation of 1-indanone. Hydrogenolysis of the carbinol XIX gave 1-(2-methoxymethylphenyl)-indan (XX) and *o*-(1-indanyl)-toluene (XXI). Formation of the toluene XXI could be minimized by first dehydrating the carbinol XIX to the indene XXII. Hydrogenation of the double bond now proceeded much more rapidly than hydrogenolysis of the benzyl ether, and although some of the toluene XXI still was obtained, the desired 1-(2-methoxymethylphenyl)-indan (XX) was isolated in 34% yield from 1-bromo-2-methoxymethylbenzene.

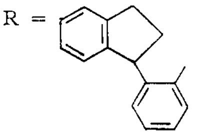


The indans and indene XIX, XX, XXI and XXII may be readily identified and the composition of their mixtures estimated by examination of their distinctive n.m.r. spectra. In XIX rotation around the bond between the benzene ring and the methoxymethyl group is sufficiently hindered to make the methylene protons non-equivalent, as shown by a quartet centered at 5.40 τ (J = 11 c.p.s.).[10] The hydroxyl proton appears at 5.92 τ and the methoxyl protons at 6.64 τ. The indan XX has a singlet at 5.60 τ for the methylene protons of the methoxymethyl group, a singlet at 6.80 τ for the methoxyl protons, and a triplet for the 1-indanyl hydrogen at 5.48 τ. The aromatic methyl group protons of XXI appear as a conspicuous sharp singlet at 7.61 τ, even when present in small concentration. The spectrum of XXII shows the expected pattern of a triplet at 4.75 τ for the vinyl proton, a doublet at 6.63 τ for the methylene protons of the indene ring and singlets at 5.83 and 6.85 τ for the protons of the methoxymethyl group.

To convert the methoxymethyl group to amino, 1-(2-methoxymethylphenyl)-indan (XX) was taken through the following series of transformations

$$\begin{tikzcd}
\mathrm{RCH_2OCH_3} \arrow[r, "\mathrm{HBr}", "\mathrm{HOAc}"'] & \mathrm{RCH_2Br} \arrow[r, "\mathrm{AgNO_3}"] \arrow[rdd, "(\mathrm{CH_3})_2\mathrm{CHNO_2}", "^{-}\mathrm{OC_2H_5}"'] & \mathrm{RCH_2ONO_2} \arrow[dd, "\mathrm{OH^-}", "\mathrm{dioxane}"'] \\
\mathrm{XX} & \mathrm{XXIII} & \mathrm{XXIV} \\
 & & \mathrm{RCHO}\ \ \mathrm{XXV} \arrow[d] \\
\mathrm{RNH_2} & \mathrm{RCOOH} \arrow[l] & \mathrm{RCH{=}NOH} \arrow[l] \\
\mathrm{XXIX} & \mathrm{XXVIII} & \mathrm{XXVII}
\end{tikzcd}$$

R =



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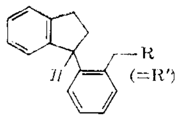
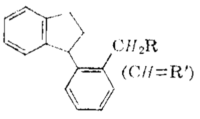
[9] (a) F. G. Hollimann and F. G. Mann, *J. Chem. Soc.*, 737 (1942); (b) F. F. Blicke and O. J. Weinkauff, *J. Am. Chem. Soc.*, **54**, 1446 (1932).

[10] J. D. Roberts "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 71.

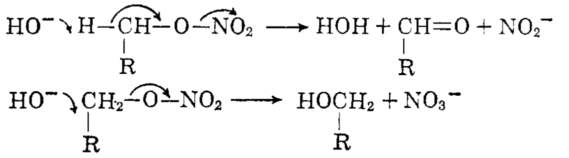
Table I

Nuclear Magnetic Resonance Absorption of Some 1-Phenylindans

Compound	R or R′		
XXI	—H	$5.35^{a,b}$	7.50
XX	—OCH_3	5.48	5.60
XXIII	—Br	5.36	5.48
XXIV	—ONO_2	5.50	4.52
XXVI	—OH	5.42	5.42
XXV	=O	4.75	-0.05^c
XXVII	=NOH	5.33	1.54

[a] Center of a triplet, as are the rest of the values in this column. [b] τ Values. [c] Changes with concentration; average value.

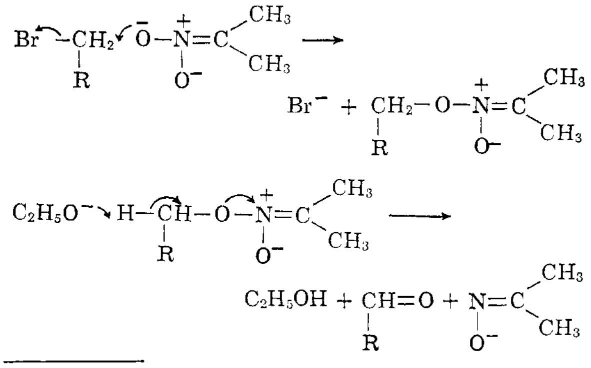
Treatment of *o*-(1-indanyl)-benzyl bromide (XXIII) with silver nitrate gave *o*-(1-indanyl)-benzyl nitrate (XXIV) which was hydrolyzed in alkaline aqueous dioxane[11] to the desired *o*-(1-indanyl)-benzaldehyde (XXV), containing some *o*-(1-indanyl)-benzyl alcohol (XXVI) resulting from simple displacement. This is not surprising in view of the mechanism formulated for the reaction of aliphatic nitrate esters with base.[12] But a comparison of the n.m.r. spectrum of the nitrate ester XXIV with those of other compounds in the series (Table I) shows clearly the increased acidity of the methylene protons due to the strong electron-withdrawing effect of the nitrate group which allows hydrogen abstraction to predominate over displacement.



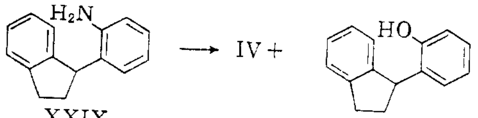
$$HO^- \; H{-}\underset{R}{CH}{-}O{-}NO_2 \longrightarrow HOH + \underset{R}{CH}{=}O + NO_2^-$$

$$HO^- \; \underset{R}{CH_2}{-}O{-}NO_2 \longrightarrow \underset{R}{HOCH_2} + NO_3^-$$

More satisfactory is the reaction of the benzyl bromide with 2-nitropropane and sodium ethoxide in ethanol.[13] The mechanism of the reaction is probably similar to that of the nitrate ester decomposition, but the greatly increased acidity of the benzylic hydrogens would result in much less displacement. Attempted preparation of the aldehyde XXV by conversion of the benzyl bromide XXIII to the tosylate and oxidation of the latter by dimethyl sulfoxide[14] was not successful. The aldoxime XXVII was heated with alkali in diethylene glycol[15] to give *o*-(1-indanyl)-benzoic acid (XXVIII). The yield of the benzoic acid XXVIII based on the methoxymethyl compound XX was 37% *via* the nitrate ester and 54% *via* the nitronate ester.



The preparation of *o*-(1-indanyl)-aniline (XXIX) was accomplished in 93% yield by a Curtius reaction. No effort was made to isolate any intermediates,[16] as indications were that rearrangement of the acid azide and hydrolysis of the carbamate were practically simultaneous. Ring closure proceeded through the free radical generated by the decomposition of the diazonium salt of XXIX and a 13% yield of crystalline 1,2-dihydrocyclopent[jk]fluorene (IV) was isolated by chromatography on alumina. A 67% yield of *o*-(1-indanyl)-phenol (XXX) was also isolated.



XXIX XXX

Properties.—1,2-Dihydrocyclopent[jk]fluorene (IV) shows the properties expected of a compound containing a strained, non-planar benzene ring, and it does indeed represent an intermediate case of strain between I and III. Table II presents a comparison of the ultraviolet spectra, hydrogen absorption and perbenzoic acid consumption of I, III and IV and their non-strained analogs.

1,9-Dimethylfluorene, the ideal model compound for IV since it is identically substituted yet unstrained, was prepared from 1-methylfluorenone.[17] Addition of methyllithium gave 1,9-dimethyl-9-fluorenol which was then hydrogenolyzed to 1,9-dimethylfluorene. The ultraviolet absorption of the cyclopentfluorene IV shows the expected slight bathochromic shift and lowered extinction coefficient, compared to 1,9-dimethylfluorene (Fig. 1), characteristic of a strained benzene ring.[3]

The nuclear magnetic resonance absorption of IV shows a distinct change from the non-ring closed 1-phenylindans (see Table I). The C_{2a}-methine hydrogen absorption of IV has shifted to higher field, 6.00 τ (indicating increased electron density on the carbon), and is split into a quartet by the adjacent methylene protons instead of a triplet (indicating that the system has become more rigid).

Additional evidence of strain in the bis-cyclopent-fused benzene ring of IV is demonstrated by its olefinic-like reactions. Hydrogen absorption (three moles) over a palladium-on-carbon catalyst proceeds rapidly at room temperature to give a

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(11) R. L. Letsinger and J. D. Jamison, *J. Am. Chem. Soc.*, **83**, 193 (1961).

(12) J. W. Baker and T. G. Heggs, *J. Chem. Soc.*, 616 (1955), and preceding papers noted therein.

(13) H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949); A. T. Bloomquist, R. E. Stahl, Y. C. Meinwald and B. H. Smith, *J. Org. Chem.*, **26**, 1687 (1961).

(14) N. Kornblum, W. J. Jones and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959).

(15) H. Rapoport and W. Nilsson, *J. Org. Chem.*, **27**, 629 (1962)

(16) *Cf.* ref. 3c.

(17) W. C. Lathrop and P. A. Goodwin, *J. Am. Chem. Soc.*, **65**, 363 (1943).

TABLE II

COMPARISON OF PROPERTIES OF STRAINED AROMATIC HYDROCARBONS AND THEIR NON-STRAINED ANALOGS

Compound	Structure	Long wave length absorption maximum, mμ (ε)	Hydrogen absorption, mole %	Perbenzoic acid consumption, mole %
2,2a,3,4-Tetrahydro-1H-cyclopent[cd]indene (I)[a]		277 (630)[b]	300	50
2a,3,4,5-Tetrahydroacenaphthene[a]		274 (710)[b]	0	50
2,2a,3,3a,4,5-Hexahydro-1H-cyclopent[jkl]-*as*-indacene (II)[c]		287 (470)[d]	300	285
1,2,3,6,7,8-Hexahydro-*as*-indacene[c]		279 (900)[d]	0	17
1,2-Dihydrocyclopent[jk]fluorene (IV)		304 (5000)[b]	273	213
1,9-Dimethylfluorene		301 (8150)[b]	0	46
Fluoradene (III)[e]		331 (4630)[d]	280	422
1-Phenylfluorene[e]		302 (4570)[d]	0	..
9-Phenylfluorene[e]		304 (10,300)[d]	0	49

[a] Ref. 3a. [b] In ethanol. [c] Ref. 3b. [d] In hexane. [e] Ref. 3c.

compound with an indan-like ultraviolet spectrum,[3c] which is presumably 1,2,6b,7,8,9,9a,9b-octahydrocyclopent[jk]fluorene (XXXI). On oxidation with perbenzoic acid, IV consumes two moles of peracid, in contrast to III, which consumes four moles, II which consumes three, and I which essentially does not react.[3]

Thus, in both its spectral properties and chemical reactions, 1,2-dihydrocyclopent[jk]fluorene (IV) reflects the presence of a strained, non-planar benzene ring. Qualitatively, based on reactivity with oxygen and perbenzoic acid, the four cyclopent compounds of this series can be placed in the following order of decreasing strain: II > III > IV > I.

Experimental[18]

3-Oxo-1,2,3,10b-tetrahydrofluoranthene (VII).—A solution of 35 g. (0.147 mole) of fluorene-9-propionic acid[5] and approximately 700 g. of anhydrous hydrogen fluoride in a loosely stoppered polyethylene bottle was allowed to evaporate slowly (approximately 40 hours) at room temperature. The residue was taken up in benzene and the resulting solution was washed well with water and then with two 50-ml. portions of 1 *N* sodium carbonate solution. Upon evaporation of the dried benzene solution, 27.6 g., 85%, of crystalline ketone was obtained having a melting point of 96–97° (reported m.p. 99–100°,[6a] 98–99°[6b]).

3-Acetoxy-1,10b-dihydrofluoranthene (IX).—3-Oxo-1,2,3-10b-tetrahydrofluoranthene (VII) (22 g., 0.1 mole), *p*-toluenesulfonic acid monohydrate (1.9 g., 0.01 mole) and 100 ml. of isopropenyl acetate were maintained at reflux for 72 hours, using an 80° condenser.[19] The isopropenyl acetate was removed at reduced pressure, the residue was dissolved in chloroform, and the chloroform solution was washed successively with saturated potassium carbonate solution and water. Evaporation of the dried chloroform solution left crude material which was crystallized from ethanol, giving 22.8 g., 87% yield, m.p. 86–88°. Recrystallization and sublimation (85° (5μ)), gave enol-acetate of m.p. 87.6–88.4°; infrared absorption: λ_{max} 5.68(s) μ; ultraviolet absorption: 268 mμ (ε 27,050), 313 (3,730), 326 (3,240).

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.4; H, 5.4; CH_3CO, 16.4. Found: C, 82.5; H, 5.3; CH_3CO, 16.1.

1-Carboxyfluorene-9-acetaldehyde (X).—Ozone was bubbled through a solution of 5 g. (19 mmoles) of enol acetate IX in 200 ml. of ethyl acetate at −70 to −75° until the original yellow solution changed to a deep blue. (With a flow rate of approximately 0.44 mmole of ozone per minute, this required 65 minutes.) The ozonized solution was added dropwise to an equal volume of boiling water, and approximately 150 ml. of the ethyl acetate was removed by steam distillation. The organic phase was separated from the cooled mixture, the aqueous phase was extracted with four 25-ml. portions of ethyl acetate, the combined ethyl acetate extracts were extracted with 1 *N* sodium carbonate solution, and the aldehydo acid was then precipitated with hydrochloric acid. The aldehydo acid was sublimed (170° (5μ)) and crystallized from ethanol–water; m.p. 181–183°, yield 2.7 g., 56%; ultraviolet absorption: 246 mμ (ε 12,890), 266 (16,260), 311 (4,550).

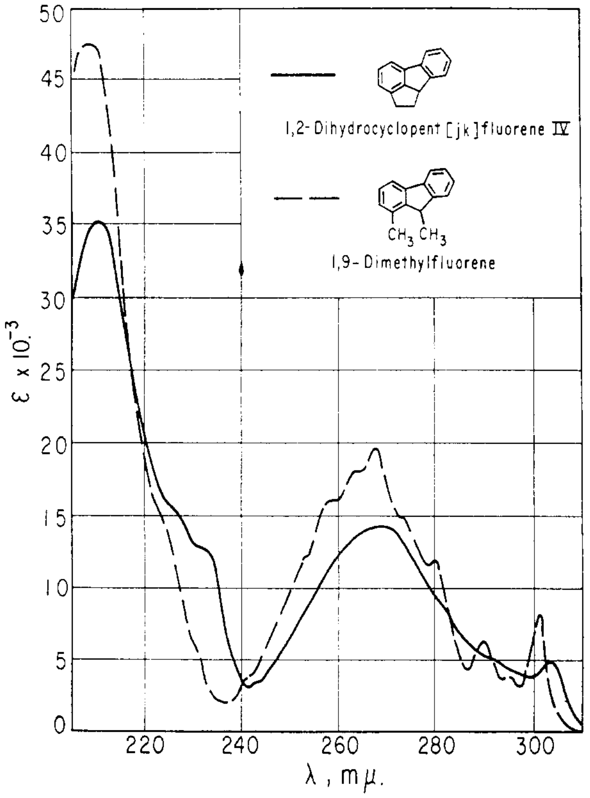

Fig. 1.—Ultraviolet absorption spectra in ethanol.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8; equiv. wt., 252. Found: C, 75.8; H, 5.0; equiv. wt., 254.

1-Carboxyfluorene-9-acetic Acid (V).—A solution of 9.81 g. (0.039 mole) of 1-carboxyfluorene-9-acetaldehyde (X), 8.81 g. of 30% hydrogen peroxide (0.078 mole) and 400 ml. of glacial acetic acid was maintained at reflux for 1 hour after which time 50 mg. of 5% palladium-on-carbon was added to the hot solution to decompose the remaining hydrogen peroxide. After the solution was filtered, the

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(18) Melting points were taken on a Kofler hot-stage; microanalyses were by V. Tashinian, Microchemical Laboratory, University of California, Berkeley. Ultraviolet spectra were taken in ethanol with a Cary model 11 or 14 recording spectrophotometer, infrared spectra were taken in chloroform with a Baird spectrophotometer, and nuclear magnetic resonance spectra were taken in carbon tetrachloride with a Varian model A-60 spectrometer, unless otherwise noted.

(19) A. L. Wilds in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 197.

glacial acetic acid was removed at reduced pressure, and the residue was heated at reflux overnight with 80 ml. of 2 *N* 50% aqueous alcoholic potassium hydroxide. The ethanol was distilled, the cooled alkaline solution was washed with ether, and the diacid was precipitated from the hot aqueous solution by addition of concd. hydrochloric acid. The precipitated acid was dried, digested for 2 hours with 70 ml. of refluxing chloroform, and the chloroform mixture was cooled in an ice-bath and filtered. Crystallization of the chloroform-insoluble material from ethanol–water gave 7.06 g. (68% yield) of diacid, m.p. 223–225°; ultraviolet absorption: 247 mμ (ε 12,500), 266 (16,000), 309 (4,150); in ethanolic alkali: 268 mμ (ε 16,000), 305 (4,690).

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5; equiv. wt., 134. Found: C, 71.8; H, 4.7; equiv. wt., 136.

Dimethyl 1-Methoxycarbonylfluorene-9-malonate (XIII). To a hot solution of potassium (1.34 g., 34 mmoles) and dimethyl malonate (8.5 ml., 62 mmoles) in 100 ml. of *t*-butyl alcohol was added methyl 9-bromofluorene-1-carboxylate[7] (9.5 g., 31 mmoles) with vigorous stirring, and the mixture was heated and stirred under nitrogen at reflux overnight. Most of the *t*-butyl alcohol was distilled, chloroform and 1 *N* hydrochloric acid were added, and the chloroform layer was washed with acid and then with 5% sodium bicarbonate solution and evaporated. Addition of ether to the residue gave colorless crystals (9.03 g., 82% yield), m.p. 111–112°.

Anal. Calcd. for $C_{20}H_{18}O_6$: C, 67.8; H, 5.1; OCH_3, 67.6; H, 5.3; OCH_3, 26.4.

A mixture of 9.03 g. (25 mmoles) of dimethyl 1-methoxycarbonylfluorene-9-malonate (XIII) and 25 ml. of 4 *N* sodium hydroxide was heated at reflux overnight with stirring. The resulting yellow solution was washed twice with chloroform, filtered, and acidified to give **1-carboxyfluorene-9-carboxylic acid (V)** which was sublimed at 200° (50 μ); yield 6.33 g., 96%, m.p. 230–232° (*cf.* m.p. 223–225° above).

Lead Salt of 1-Carboxyfluorene-9-acetic Acid (V).—A paste was made of 10.10 g. (38 mmoles) of 1-carboxyfluorene-9-acetic acid (V) and 35 ml. of ethanol, and 1 *N* sodium hydroxide was added until the *p*H reached 7.5. The solution was filtered, 150 ml. of warm 0.42 *M* lead nitrate solution was added over 3 hr. with vigorous stirring, and the precipitated lead salt was washed twice with ethanol then twice with water. Drying overnight *in vacuo* at 100° gave 16.63 g. of white powder.

Anal. Calcd. for $C_{16}H_{10}O_4Pb$: C, 40.6; H, 2.1; Pb, 43.8. Found: C, 41.0; H, 2.4; Pb, 43.7.

Pyrolysis of the Lead Salt of 1-Carboxyfluorene-9-acetic Acid (V).—In a typical experiment, 2.00 g. (4.2 mmoles) of the lead salt of V was pyrolyzed at 370° (5–10 mm.) for 6 hr. The pyrolysate was dissolved in chloroform and the solution was extracted with sodium bicarbonate solution. This aqueous phase was acidified and extracted with ether. Evaporation of the ether left a residue which was sublimed at 100° (5 μ) and crystallized from benzene to give **9-methylfluorene-1-carboxylic acid (XIV)**,[20] m.p. 196–197°; ultraviolet absorption: λ_{max} 246 mμ (ε 13,870), 265 (17,200), 311 (5,240); in ethanolic alkali: λ_{max} 265 (ε 17,900), 304 (5660); nuclear magnetic resonance absorption[21]: C_9–CH_3, 8.60 τ (doublet); C_9–H, 5.64 τ (quartet).

Anal. Calcd. for $C_{15}H_{12}O$: C, 80.3; H, 5.4; equiv. wt., 224. Found: C, 80.2; H, 5.5; equiv. wt., 222.

The filtered chloroform phase was now evaporated, the residue was digested with benzene and filtered, and the filtrate was evaporated. This residue was divided into an ether-soluble portion and an ether-insoluble portion by digestion with ether. The ether-insoluble fraction was crystallized from benzene–hexane and gave 200 mg., 13% yield, of **di-1-(9-methylfluorenyl)ketone (XV)**, m.p. 254–256°; ultraviolet absorption λ_{max} 233 (ε 36,100), 256 (46,400), 277 sh (31,400), 290sh (14,600), 298sh (10,400), 327 (6,330).

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.1; H, 5.7. Found: C, 90.2; H, 5.6.

The ether-soluble fraction was chromatographed on alumina (acid-washed, activity I), eluting with hexane and hexane-benzene. Fractions eluted with hexane–benzene (65:35) were combined and triturated with ether. Evaporation of the ether solution left 5 mg. of **fluorenone**, identical with an authentic sample in m.p., mixed m.p. and ultraviolet absorption. The ether-insoluble portion was an orange powder which could not be separated into any pure components by further chromatography.

Experiments with Radioactive Compounds.—In exactly the same manner as described above, dimethyl 1-methoxycarbonylfluorene-9-[α-^{14}C]-malonate (XIII) and 1-carboxyfluorene-9-[α-^{14}C]-acetic acid (V) were prepared from methyl 9-bromofluorene-1-carboxylate and dimethyl [α-^{14}C]-malonate. The lead salt of V was prepared and pyrolyzed as described, giving the same products as above. Liquid scintillation counting gave the following activities:

Compound	Specific activity, μc./mmole
Dimethyl 1-methoxycarbonylfluorene-9-[α-^{14}C]-malonate (XIII)	1.18
1-Carboxyfluorene-9-[α-^{14}C]-acetic acid (V)	1.16
Di-1-(9-methyl-^{14}C-fluorenyl) ketone (XV)	2.22

Lead Salt of 9-Methylfluorene-1-carboxylic Acid (XIV).—9-Methylfluorene-1-carboxylic acid (XIV) (539 mg., 2.4 mmoles) was dissolved in 5 ml. of ethanol and sufficient 0.1 *N* sodium hydroxide was added to achieve a *p*H of 7.5. This solution was then filtered. A slow addition (*ca.* 1 hour) of lead nitrate solution (785 mg., 2.4 mmoles, in 20 ml. of water) to the filtrate with vigorous stirring precipitated the lead salt of the acid. The precipitate was filtered, washed with water (2 × 25 ml.) and alcohol (2 × 50 ml.), and dried at 100°(0.1 mm.), yield 696 mg., 88%.

Pyrolysis of the Lead Salt of 9-Methylfluorene-1-carboxylic Acid (XIV).—The lead salt (696 mg., 1.07 mmoles) was heated in a sublimation apparatus for 3 hr. at 250° (5 mm.), and the sublimate was removed from the cold finger with benzene. This material (100 mg., 21%) was shown to be entirely 9-methyl-1-fluorenecarboxylic acid. Continuation of the pyrolysis at 300° (5 mm.) for 5 hours gave additional sublimate which was dissolved in benzene, and the benzene solution was washed with 1 *N* potassium carbonate, dried and evaporated. The residue was chromatographed on 8 g. of acid-washed alumina, using hexane for elution. From the combined fractions 4–6 (25-ml. fractions), 101 mg. (24%) of di-1-(9-methylfluorenyl) ketone (XV) was obtained which, after crystallization from benzene–hexane, melted at 254–257° and was identical in infrared and ultraviolet absorption and m.p. and mixed m.p. with the ketone obtained from the pyrolysis of the lead salt of 1-carboxyfluorene-9-acetic acid (V).

Di-1-(9-methylfluorenyl)-methane (XVI).—A mixture of 198 mg. (0.51 mmole) of di-1-(9-methylfluorenyl) ketone (XV), 50 ml. of glacial acetic acid and 120 mg. of 5% palladium-on-charcoal was stirred in a hydrogen atmosphere until hydrogen absorption ceased (*ca.* 20 hours). An additional 100 mg. of catalyst was added and the hydrogenation continued. This procedure was repeated once more. The solution was filtered, the catalyst was digested with benzene, and the residue from evaporation of the acetic acid–benzene solution was found to be a mixture of alcohol and ketone as shown by its infrared spectrum. This alcohol–ketone mixture was boiled with 0.5 g. of lightly amalgamated zinc dust, 3 g. of granulated zinc, 90 ml. of glacial acetic acid and 10 ml. of concentrated hydrochloric acid for 9 hours. The cooled solution was diluted with 350 ml. of water and extracted with three 50-ml. portions of benzene. The combined benzene extracts were washed with 1 *N* sodium hydroxide, dried and evaporated. Crystallization of the residue from benzene–methanol gave 133 mg., 70% yield, of hydrocarbon, m.p. 246–247°; ultraviolet absorption: λ_{max}^{hexane} 269 mμ (ε 45,100), 291 (16,400), 304 (23,000).

Anal. Calcd. for $C_{29}H_{24}$: C, 93.5; H, 6.5. Found: C, 93.9; H, 5.9.

1-(2-Chlorophenyl)-indan (XVII).—*o*-Chlorobromobenzene (58.5 g., 0.306 mole) in 160 ml. of ether was added dropwise with stirring to 7.4 g. (0.306 mole) of magnesium in 30 ml. of ether. Indanone (27 g., 0.205 mole) in 20 ml. of benzene and 75 ml. of ether was stirred into the Grignard reagent. The solution was boiled for 1 hour after which it was poured onto 50 ml. of acetic acid and cracked ice. The

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[20] The yield of this acid in various pyrolyses ranged from traces to 6%.

[21] Since the acid XIV is insoluble in carbon tetrachloride, this measurement was made on the acid chloride, prepared by heating the acid with thionyl chloride.

organic phase was washed with sodium hydroxide solution and evaporated leaving a residue which was boiled 4 hours with lightly amalgamated zinc dust (24 g.), granulated zinc (48 g.), 1300 ml. of acetic acid and 280 ml. of concd. hydrochloric acid. Diluting with 1000 ml. of water, extracting with benzene, washing the benzene extract with sodium hydroxide solution, and evaporating the benzene left a residue which was distilled at reduced pressure. The 1-(2-chlorophenyl)-indan (XVII) fraction, boiling between 110–140°(0.6–0.3 mm.), weighed 32.6 g., 47% yield.

Anal. Calcd. for $C_{15}H_{13}Cl$: C, 78.8; H, 5.7; Cl, 15.5. Found: C, 78.7; H, 5.6; Cl, 15.4.

1-(2-Methoxymethylphenyl)-1-indanol (XIX).—A solution of 34.0 g. (0.17 mole) of 1-bromo-2-methoxymethylbenzene,[9a] prepared from *o*-bromobenzyl bromide,[22] in 100 ml. of tetrahydrofuran was added to 4.1 g. (0.17 mole) of magnesium (activated with iodine) in 35 ml. of tetrahydrofuran in a nitrogen atmosphere at 60° with stirring. Formation of the Grignard reagent was initiated with ethylene dibromide. After all the magnesium had dissolved, a solution of 24.5 g. (0.187 mole) of indanone in 170 ml. of tetrahydrofuran was added over 3 hr. After being stirred at reflux for 2 hr. and at room temperature overnight, the tetrahydrofuran was evaporated *in vacuo* and chloroform and 100 ml. of 2 *N* acetic acid were added. The organic phase was separated, the aqueous phase was extracted with chloroform, and the combined chloroform extracts were washed with water and 5% sodium bicarbonate solution. Evaporation of the dried chloroform left 41.1 g. of an oil.

Methanol was added to this oily residue and the solution was cooled at −15° overnight. The resulting crystals (7.2 g.) were washed with cold methanol, crystallized from ethanol, and sublimed (130° (0.1 mm.)) to give **2-(1-indanylidene)-1-indanone, XVIII)**, m.p. 142–143° (reported[23] m.p. 142–143°); ultraviolet absorption: λ_{max} 247 mμ (ϵ 10,150), 343 (31,400); infrared absorption: λ_{max} 6.02, 6.25, 6.35, 7.56, 10.07 μ.

The methanol mother liquors were evaporated and the residue, dissolved in benzene, was chromatographed on neutral alumina. Elution with chloroform–benzene (1:1) gave more 2-(1-indanylidene)-1-indanone and this was followed by **1-(2-methoxymethylphenyl)-1-indanol (XIX)**, eluted with chloroform–benzene, 3:1. Crystallization from hexane and sublimation (110°(0.1 mm.)) gave material melting at 80–81°; ultraviolet absorption: λ_{max} 259 mμ (ϵ 1100), 264 (1430), 272 (1380); infrared absorption: λ_{max} 2.95, 6.26, 6.76, 6.91, 7.25, 8.38 μ; nuclear magnetic resonance absorption: $-CH_2O-$, 5.40 τ (quartet); –OH, 5.92; $-OCH_3$, 6.64.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1; OCH_3, 12.2. Found: C, 80.3; H, 7.4; OCH_3, 11.9.

1-(2-Methoxymethylphenyl)-indan (XX).—A solution of 1.69 g. (6.7 mmoles) of the indanol XIX in 100 ml. of absolute ethanol was shaken with hydrogen at room temperature and 30 p.s.i. pressure in the presence of 0.2 g. of 10% palladium-on-carbon until 100 mole % of hydrogen had been absorbed. The mixture was filtered, the filtrate was evaporated *in vacuo*, and the residue was distilled in a short-path apparatus at b.p. 100° (0.2 mm.), yield 1.47 g., 93%; ultraviolet absorption: λ_{max} 260 mμ (ϵ 1250), 266 (1530), 273 (1420); infrared absorption: λ_{max} 3.38, 6.26, 6.76, 6.89, 7.24, 8.41, 9.15 μ; nuclear magnetic resonance absorption: C_1–H, 5.48 τ (triplet); $-CH_2O-$, 5.60 τ; OCH_3, 6.80 τ.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6; OCH_3, 13.0. Found: C, 85.6; H, 7.5; OCH_3, 11.9.

The same product could be obtained by first dehydrating the indanol XIX and then hydrogenating. Dehydrogenation was accomplished by boiling in a nitrogen atmosphere a solution of the indanol XIX in benzene containing a catalytic amount of *p*-toluenesulfonic acid and using a water separator. The solution was washed with sodium bicarbonate solution (5%), dried, and evaporated to yield **1-(2-methoxymethylphenyl)-1-indene (XXII)** as an oil; ultraviolet absorption: λ_{max} 250 (sh) mμ (ϵ 9,400).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.4; H, 6.8. Found: C, 85.8; H, 7.1.

This oil was hydrogenated as in the preparation of the indane XX above, and 100 mole % of hydrogen was absorbed in 0.5 hr. Filtration, evaporation and short-path distillation gave **1-(2-methoxymethylphenyl)-indan (XX)** in practically quantitative yield.

The best over-all yields were obtained in the following way: A solution of the total product from the Grignard reaction described above was treated as described to remove 2-(1-indanylidene)-indanone (XVIII). The residue was boiled in benzene containing *p*-toluenesulfonic acid until no more water separated, and the benzene solution was washed with bicarbonate solution (5%), dried, and evaporated. The residue from the benzene solution was hydrogenated as above, and the hydrogenation product was chromatographed on neutral alumina (activity I). Hexane eluted a small amount of *o*-**(1-indanyl)-toluene (XX)**, purified as an oil by short-path distillation (60° (1 mm.)) (reported[24] m.p. 57°); ultraviolet absorption: λ_{max} 260 mμ (ϵ 1300), 266 (1420), 273 (1350); nuclear magnetic resonance absorption: C_1–H, 5.35 τ (triplet); CH_3, 7.50 (singlet).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.3; H, 7.7. Found: C, 91.6; H, 7.8.

Continued elution with benzene removed a mixture of the indene XXII and the indan XX. This mixture was again hydrogenated to give a 34% over-all yield from 1-bromo-2-methoxymethylbenzene to 1-(2-methoxymethyl phenyl)-indan (XX).

o-**(1-Indanyl)-benzoic Acid (XXVIII). A.** ***Via*** **Nitrate Ester.**—A solution of 4.5 g. (19 mmoles) of 1-(2-methoxymethylphenyl)-indan (XX) in 75 ml. of 30% hydrogen bromide in acetic acid was heated on the steam-bath for 4 hr., and then poured into 100 ml. of water and extracted with ether. The ether solution was washed with water (3 × 50 ml.) and 5% sodium bicarbonate solution (2 × 50 ml.), dried, and evaporated to leave a residue of *o*-**(1-indanyl)-benzyl bromide (XXIII)**. This oily residue was dissolved in 300 ml. of dioxane and a solution of 12.6 g. (74 mmoles) of silver nitrate in 20 ml. of water was added. After being stirred for 4 hr., the mixture was filtered, and the filtrate was evaporated to a residue which was dissolved in ether. The ether was washed with water, dried, and evaporated to leave the *o*-**(1-indanyl)-benzyl nitrate (XXIV)** (infrared absorption: λ_{max} 6.15, 7.32 μ) as an oily residue which was dissolved in 300 ml. of dioxane and heated under reflux in a nitrogen atmosphere with a solution of 13.5 g. of potassium hydroxide in 30 ml. of water. The solution was concentrated to a small volume, water and ether were added, and the ether phase was dried and evaporated, leaving a residue of *o*-**(1-indanyl)-benzaldehyde (XXV)** (infrared absorption: λ_{max} 5.99 μ).

The oxime was prepared by boiling overnight a solution of this crude aldehyde in 40 ml. of absolute ethanol and 40 ml. of pyridine to which 3.6 g. of hydroxylamine hydrochloride had been added. The solution was concentrated to a small volume, water and ether were added, and the ether phase was washed with 3 *N* hydrochloric acid followed by 5% sodium bicarbonate solution. Evaporation of the dried ether left 4.2 g. of the crude oxime. A sample was purified by crystallization from hexane and sublimation (80° (0.1 mm.)). *o*-**(1-Indanyl)-benzaldehyde oxime (XXVII)** melted at 119–129°; ultraviolet absorption: λ_{max} 254 mμ (ϵ 11,600).

Anal. Calcd. for $C_{16}H_{15}NO$: C, 81.0; H, 6.4; N, 5.9. Found: C, 80.4; H, 6.3; N, 5.8.

To prepare the acid XXVIII, the crude oxime was dissolved in 20 ml. of diethylene glycol and 4.0 g. of potassium hydroxide was added. The solution was heated at 180–190° for 7 hr., then poured into water. The aqueous solution was washed with ether then acidified with concd. hydrochloric acid and extracted with ether. The ether was washed thoroughly with 10% sodium bicarbonate solution,[25]

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(22) DeL. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, **78**, 475 (1956).

(23) F. S. Kipping, *J. Chem. Soc.*, **65**, 480 (1894); F. Bergmann and Y. Hirshberg, *J. Am. Chem. Soc.*, **65**, 1429 (1943).

(24) J. von Braun, G. Manz, and E. Reinsch, *Ann.*, **468**, 277 (1929).

(25) Evaporation of the ether phase after this bicarbonate wash left a residue of crude *o*-(1-indanyl)-benzyl alcohol (XXVI) (for n.m.r. see Table I). When crude oxime XXVII was used to prepare acid XXVIII, this alcohol was carried along as a contaminant. It originated from hydroxide displacement on the nitrate ester XXIV in the preparation of aldehyde XXV. The possibility that this alcohol was formed from aldehyde XXV by a Cannizzaro reaction was eliminated, since none of the corresponding acid was found.

the combined bicarbonate washes were heated to remove dissolved ether, and the cooled solution was acidified to precipitate *o*-(1-indanyl)-benzoic acid (XXVIII). Sublimation at 120° (0.1 mm.) gave 1.23 g. of material, m.p. 148–149°, 37% over-all yield based on the methoxymethyl compound XX.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9. Found: C, 80.1; H, 5.9.

B. *Via* **Nitronate Ester.**—To a solution of 0.17 g. (7.2 mmoles) of sodium in 5 ml. of abs. alcohol were added 0.9 ml. (10 mmoles) of 2-nitropropane and a solution of 1.45 g. (5 mmoles) of crude *o*-(1-indanyl)-benzyl bromide (XXIII) in 10 ml. of abs. ethanol. The mixture was stirred for 24 hr., then it was filtered and the filtrate was evaporated. Water and ether were added, the ether layer was washed with water and 2 *N* sodium hydroxide, dried, and evaporated, and the residue of crude aldehyde (1.10 g.) was converted to oxime and acid as above. The yield of sublimed acid XXVIII was 0.65 g., 54% yield based on the benzyl bromide XXIII.

***o*-(1-Indanyl)-aniline** (XXIX).—Thionyl chloride (6.5 ml.) was added to 1.23 g. (5.2 mmoles) of *o*-(1-indanyl)-benzoic acid (XXVIII) and the mixture was stirred at 45–50° for 2 hr. The thionyl chloride was evaporated and to the resulting oil were added 72 ml. of cold acetone, 0.43 g. (7.8 mmoles) of activated sodium azide[26] in 1.8 ml. of water and enough ice-water to give a solution which was stirred in the ice-bath for 2 hr. Water (200 ml.) was added, the solution was extracted four times with ether, and the ether was washed with water, dried, and evaporated. Boiling the residue in 40 ml. of abs. ethanol for 2 hr. was followed by addition of 2.0 g. of potassium hydroxide and an overnight reflux. The ethanol was evaporated, the residue was distributed between water and ether, the ether was washed with 2 *N* hydrochloric acid, and the acid phase was made strongly alkaline and extracted with ether. The residue on evaporation of the ether was distilled onto a cold finger (b.t. 90° (0.1 mm.)); yield 1.0 g., 93%; ultraviolet absorption: λ_{max} 236 mμ (ϵ 8000), 267 (2100), 273 (2640), 287 (2740); in ethanolic hydrochloric acid, λ_{max} 267 mμ (ϵ 1400), 273 (1280); infrared absorption: λ_{max} 2.93, 3.01, 6.22, 6.34, 6.70, 6.77, 6.89, 7.82 μ.

Anal. Calcd. for $C_{15}H_{15}N$: C, 86.1; H, 7.2; N, 6.7. Found: C, 86.0; H, 7.4; N, 6.9.

1,2-Dihydrocyclopent[jk]fluorene (IV).—A solution of 1.34 g. (6.4 mmoles) of *o*-(1-indanyl)-aniline (XXXIX) in 25 ml. of acetic acid and 0.45 ml. of concd. sulfuric acid was cooled to 10–15° with stirring. A solution of 0.51 g. (7.4 mmoles) of sodium nitrite in 4.7 ml. of water was added under the surface over 15–20 min. The solution was diluted with 87 ml. of cold 3 *N* sulfuric acid and sulfamic acid was added until starch–potassium iodide paper showed a negative test for nitrous acid. The mixture was heated under nitrogen at 90–100° with stirring for 1 hr. Benzene (50 ml.) was added, the organic layer was washed with water (6 × 75 ml.), and each water wash was back washed with the same 50 ml. of benzene. The benzene layers were combined, dried, and evaporated to leave 1.35 g. of oil. Chromatography on 67 g. of acid-washed alumina (activity I) gave 24 mg. of unidentified material with 175 ml. of hexane, 166 mg. (13% yield) of crystalline product with 400 ml. of hexane, and later fractions eluted with benzene–chloroform which were mainly *o*-(1-indanyl)-phenol (XXX). Part of the 1,2-dihydrocyclopent[jk]fluorene was sublimed (50° (0.2 mm.)) to give material melting at 44–45°; ultraviolet absorption: λ_{max} 211 mμ (ϵ 35,000), 233 (13,500), 268 (14,500), 304 (5000); nuclear magnetic resonance absorption: C_{2a}–H, 6.00 τ (quartet).

Anal. Calcd. for $C_{15}H_{12}$: C, 93.7; H, 6.3. Found: C, 93.9; H, 6.4.

The phenolic fractions (0.90 g., 67% yield) were combined and a portion was distilled (50° (0.2 mm.)) onto a cold finger to give ***o*-(1-indanyl)-phenol** (XXX) as an oil.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.6; H, 6.7.

1,9-Dimethylfluorene.—Thirty ml. (30 mmoles) of ethereal 1 *N* methyllithium was added in six equal portions with stirring to a solution of 3 g. (15.5 mmoles) of 1-methylfluorenone[17] in 80 ml. of ether. After addition was complete, the reaction was stirred for an additional 0.5 hr. and then poured onto 3 ml. of acetic acid and cracked ice. The aqueous phase was separated and the organic phase washed successively with sodium carbonate solution, water, and saturated sodium chloride solution. On evaporation of the dried ether solution, 2.93 g. (90%) of **1,9-dimethyl-9-hydroxyfluorene** was obtained. Crystallization from benzene and a sublimation (90° (5 μ)) resulted in material melting at 176–177°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.4; H, 6.8.

1,9-Dimethylfluorene was obtained by reduction of 1 g. (4.76 mmoles) of 1,9-dimethyl-9-hydroxyfluorene dissolved in 150 ml. of abs. ethanol and vigorously shaken with 200 mg. of 5% palladium-on-carbon in an atmosphere of hydrogen at 35° for 24 hr. Benzene (50 ml.) was added to bring the product into solution before removing the catalyst by filtration. The catalyst was washed thoroughly with 100 ml. of benzene, the solvents were evaporated, and the residue was crystallized from ethanol and sublimed (75° (15 mm.)), m.p. 71–72°, 100% yield; ultraviolet absorption: λ_{max} 210 mμ (ϵ 47,400), 267 (19,400), 290 (6250), 301 (8150); nuclear magnetic resonance absorption: C_1–CH_3, 7.65 τ (singlet); C_9–CH_3, 8.63 (doublet); C_9–H, 6.31 (quartet).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.7; H, 7.3. Found: C, 92.4; H, 7.5.

Hydrogenation and Peroxidation of 1,2-Dihydrocyclopent[jk]fluorene (IV). A. Hydrogenation.—1,2-Dihydrocyclopent[jk]fluorene (IV) (6.36 mg., 0.033 mmole) was hydrogenated in ethanol over 5% palladium-on-carbon. The reaction was complete in 0.5 hour after 0.090 mmole of hydrogen had been absorbed (273 mole %). The ethanol was evaporated and the sample was sublimed to give a colorless oil; ultraviolet absorption: λ_{max} 261 mμ (ϵ 780), 267 (1220), 274 (1420).

Under identical conditions, 1,9-dimethylfluorene absorbed no hydrogen.

B. **Peroxidation.**—The sample to be oxidized was weighed into a volumetric flask which was then filled with standardized perbenzoic acid solution.[27] A 100-λ aliquot was withdrawn at intervals along with a 100-λ portion of the standard perbenzoic acid solution and titrated. Both were maintained at room temperature. Titrations were done with 0.0025 *M* thiosulfate into a mixture of 5 ml. of acetic acid, 5 ml. of chloroform and 3 ml. of 0.5% potassium iodide until the pink color disappeared from the chloroform layer. The reaction was considered to be complete when the difference in titer between the sample and standard remained constant. Table III shows the results of these experiments.

TABLE III

PERBENZOIC ACID OXIDATION EXPERIMENTS

Compound	Hydrocarbon, *M*	Perbenzoic acid, *M*	Mole % consumed	Time, hr.
1,9-Dimethylfluorene	0.0186	0.063	35	46
	.0282	.159	57	24
1,2-Dihydrocyclopent-	.0313	.159	194	43
[jk]fluorene (IV)	.0313	.371	232	20

The remainder of the solution from an oxidation of 1,2-dihydrocyclopent[jk]fluorene (IV) in which 232 mole % of perbenzoic acid was consumed (see Table III) was treated with excess aqueous potassium iodide and sodium thiosulfate. The chloroform layer was separated, washed twice with 5% sodium bicarbonate, dried and evaporated. The residue was digested with hexane, and the hexane was decanted and evaporated to give an oil; ultraviolet absorption: λ_{max} 231 mμ (ϵ ~ 8600), 258 (~ 1900); infrared absorption: 2.83, 5.69, 5.85, 7.90, 8.98, 9.05, 9.95 μ.

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[26] P. A. S. Smith in "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 382.

[27] G. Braun in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 431.