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THE SYNTHESIS OF FLUORANTHENE DERIVATIVES[1]

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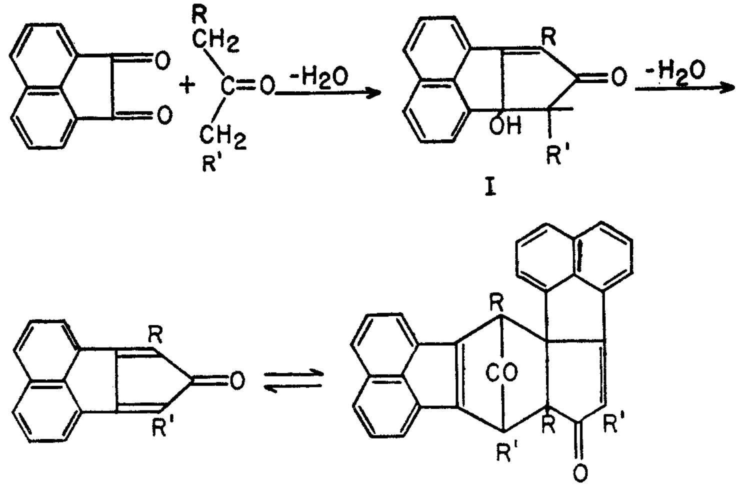
No simple way has yet been reported for preparing fluoranthene derivatives containing alkyl or aryl groups in which the position of the substituent is known. Most syntheses of fluoranthenes so far described (1, 2) require several steps. It has been found that the most suitable procedure is that of Dilthey (2) who treated acecyclone (III; R, R′ = C_6H_5) with maleic anhydride, and obtained the anhydride of 7,10-diphenylfluoranthene-8,9-dicarboxylic acid. Extension and modification of this procedure has led to the formation of a large number of new substituted fluoranthenes (VI), in which all the substituent groups are in the left-hand ring.

The starting material is acenaphthenequinone, which is condensed with various alkyl ketones at 25–30° in methanol with an alkaline catalyst. As with benzil (3), three types of products result. Methyl *n*-alkyl ketones, in general, give carbinols (I) which, upon dehydration, do not give substituted cyclopentadienones but non-reversible dimers. Other ketones, however, give carbinols which may be dehydrated to a reversible dimer (II) or the corresponding monomeric cyclopentadienone (III). In some instances, the carbinol is unstable, even at 25–50° under the conditions of the condensation, so that the dienone results directly. The carbinols that are stable at room temperatures may also be converted to the cyclopentadienone by refluxing in alkaline solution. All these points of behavior were noted in our previous paper on simple substances (3).



I

III

II

The structure of the dimer (II) has not been proved, but is written as shown

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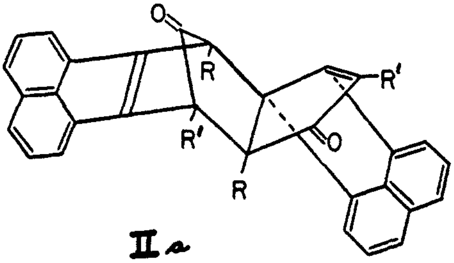
because it gives the same types of reactions as the previously described, simpler substances (3) of known structure. A planar projection of this dimer would indicate considerable overcrowding of the various groups. Actually, this is not the case, as examination of the perspective drawing (IIa) will show.



IIa

In this drawing an endo relation of the bridge ketone to the five-membered ring containing the other keto group, and the *cis* type of addition have been assumed. Since this is the usual mode of addition (8), the number of isomerides is thus limited. The limiting factor in the formation of a dimeride in this series is the size of the R group. If R is isopropyl or phenyl, a dimeride is not formed.

TABLE I

PROPERTIES OF THE REVERSIBLE DIMERS II[i]

R	R'	M.P., °C.	YIELD, %	EMPIRICAL FORMULA	ANALYSES			
					Calc'd		Found	
					C	H	C	H
CH_3[a]	CH_3	200°	56	$C_{17}H_{12}O$	87.8	5.2	88.4	5.7
C_2H_5[b]	C_2H_5	186	74	$C_{19}H_{16}O$	87.6	6.2	87.7	6.2
n-C_3H_7[b]	n-C_3H_7	157	77	$C_{21}H_{20}O$	87.4	6.9	87.7	7.0
CH_3[c]	C_6H_5	153	81	$C_{22}H_{14}O$	89.6	4.8	89.6	5.1
n-C_6H_{13}[b]	n-C_6H_{13}	105	105	$C_{27}H_{32}O$	87.2	8.6	87.2	9.0

Solvents for Tables 1–5; [a] benzene-methanol; [b] ligroin; b.p. 90–120°; [c] butanol; [d] xylene; [e] acetic acid; [f] ethanol; [g] acetic anhydride; [h] *o*-dichlorobenzene. [i] All these substances are a very pale yellow.

TABLE II

PROPERTIES OF MONOMERS III

R	R'	M.P., °C.	YIELD, %	EMPIRICAL FORMULA	ANALYSES			
					Calc'd		Found	
					C	H	C	H
i-C_3H_7[d]	i-C_3H_7[aa]	145	60	$C_{21}H_{20}O$	87.4	6.9	87.4	7.2
$COOC_2H_5$[d]	$COOC_2H_5$[bb]	196	68	$C_{21}H_{16}O_5$	72.5	4.6	72.5	4.7

[aa] Blue-black. [bb] Deep purple.

This may be regarded as being due to the inability of the reacting groups to come within bond-forming distances of each other (9).

A summary of the reversible dimers and their properties appears in Table I; the monomeric cyclopentadienones are similarly collected in Table II, while the carbinols are summarized in Table III.

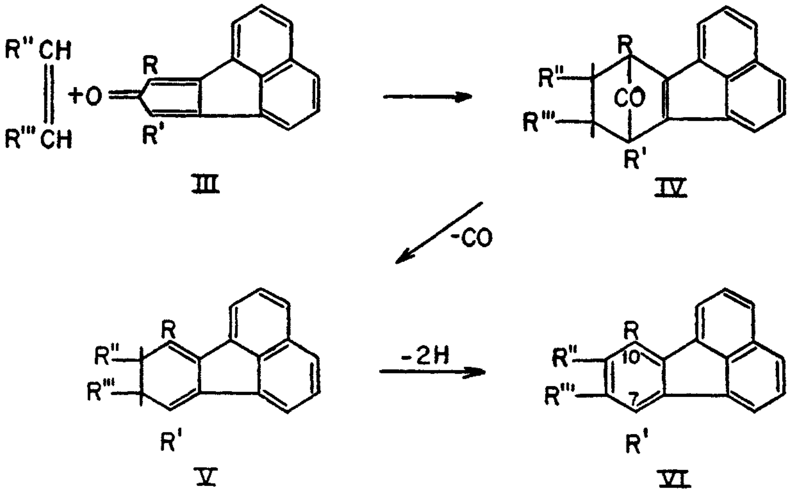
TABLE III

PROPERTIES OF CARBINOLS*

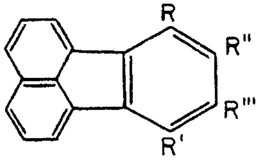
	R	R′	M.P., °C.	YIELD, %	EMPIRICAL FORMULA	ANALYSES			
						Calc'd		Found	
						C	H	C	H
Ia	CH_3^e	H	207–210	38	$C_{16}H_{11}O_2$	81.6	4.7	80.8	4.4
Ib	CH_3^c	CH_3	212	92	$C_{17}H_{14}O_2$	81.5	5.6	81.8	5.9
Ic	C_2H_5^f	C_2H_5	162	89	$C_{19}H_{17}O_2$	81.9	6.5	82.2	6.4
Id	*n*-C_3H_7^b	*n*-C_3H_7	100	75	$C_{21}H_{22}O_2$	82.4	7.2	82.6	7.4
Ie	C_6H_5	H	178	78	$C_{21}H_{14}O_2$	84.5	4.7	84.4	5.0

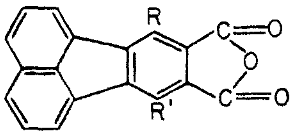
* All these compounds are white.

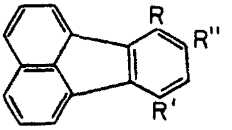
The new fluoranthene derivatives (VI) were all obtained by the addition of a suitable unsaturated compound to the monomeric cyclopentadienone; carbon monoxide was eliminated from the adduct (IV) if the addition was carried out above 45°. With acetylenic dienophiles, the completely aromatic structure (VI) was obtained at once, as would be expected (4). The use of ethylenic compounds gave dihydrofluoranthene derivatives (V); the latter were subsequently dehydrogenated by means of permanganate in acetone or by palladized carbon.

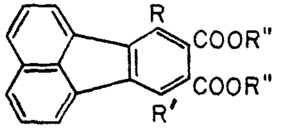


The properties of the new fluoranthenes are collected in Tables IV and V. In making comparisons of these fluoranthene derivatives, it is more convenient to employ the orientation shown in VIa, rather than the general type formula (VI). Thus, the similarity between the anhydrides (VII) and esters (VIII) is more evident when the structures are written in this way.


VIa


VII


IX


VIII

The ease with which the CO bridge is lost in the adducts (IV) is noteworthy and was not anticipated (4), even though it had occurred previously in the one known instance. Dilthey (5) noted that a temperature of 120–130° was necessary for this reaction with acecyclone itself, and attributed the decarbonylation to the high temperature as well as the greater activity of acecyclone, as compared to that of tetraphenylcyclopentadienone. We find that when the alkyl substituted dienones (III; R, R′ = alkyl) and maleic anhydride are refluxed in benzene (6) this elimination takes place. However, when the addition of III to maleic anhydride is carried out in benzene at room temperature, the endocarbonyl bridge is retained. When, for example, III (R, R′ = *n*-hexyl or R, R′ = ethyl) is added to maleic anhydride under these conditions, an adduct IV is obtained. The similarity to the tetracyclone and phencyclone series is thus complete. The endo bridge in this series is merely more labile.

TABLE IV

8,9-DIHYDROFLUOROANTHENES, V*

NO.	R	R′	R″	R‴	M.P., °C.	YIELD, %	EMPIRICAL FORMULA	ANALYSES			
								Calc'd		Found	
								C	H	C	H
V	C_6H_5[c]	C_6H_5	C_6H_5	H	165	78	$C_{34}H_{24}$	94.6	5.6	94.4	6.0
V	C_6H_5[g]	C_6H_5	4′-ClC_6H_4	H	158	74	$C_{34}H_{23}Cl$	87.6	5.0	87.4	5.5
V	C_6H_5[d]	C_6H_5	COOH	H	198–200 dec.	81	$C_{29}H_{18}O_2$	87.5	4.5	88.0	5.4

* All these compounds are yellow.

Like most other decarbonylated adducts (6), the dialkyldihydrofluoranthenes

(XI; R, R′ = alkyl) add maleic anhydride to give bis-anhydrides (X). The latter can be obtained directly from the cyclopentadienone (III) by refluxing an acetic acid solution of the latter with two equivalents of maleic anhydride.

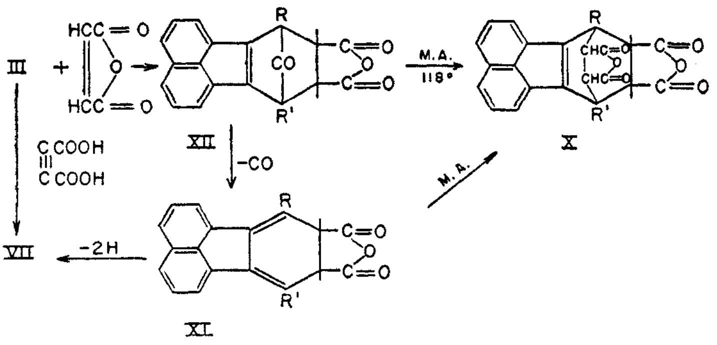
TABLE V

FLUORANTHENES, VIII*

NO.	R	R′	R″	M.P., °C.	YIELD, %	EMPIRICAL FORMULA	ANALYSES			
							Calc'd		Found	
							C	H	C	H
VIIIa	CH_3^a	C_6H_5	CH_3	163	93	$C_{27}H_{20}O_4$	79.5	4.9	79.6	5.0
VIIIb	$C_2H_5^a$	C_2H_5	CH_3	195	92	$C_{24}H_{22}O_4$	76.9	5.9	77.1	6.2
VIIIc	CH_3^b	CH_3	C_4H_9	122	88	$C_{28}H_{30}O_4$	78.2	7.0	78.3	7.2
VIIId	$C_2H_5^b$	C_2H_5	C_4H_9	94	85	$C_{28}H_{35}O_4$	78.5	7.4	78.2	7.6
VIIIe	n-$C_3H_7^b$	n-C_3H_7	CH_3	162	83	$C_{26}H_{26}O_4$	77.6	6.5	77.7	6.6
VIIIf	$C_6H_5^c$	C_6H_5	C_4H_9	155	80	$C_{38}H_{34}O_4$	82.5	6.1	82.2	6.0
IXa	C_6H_5	C_6H_5	C_6H_5	Ref. 5						
IXb	$C_6H_5^b$	C_6H_5	4-ClC_6H_4	191	69	$C_{34}H_{21}Cl$	87.9	5.2	87.8	5.1
IXc	$C_6H_5^b$	C_6H_5	CH_2OH	156–158	61	$C_{28}H_{20}O$	90.4	5.4	91.0	5.8
IXd	$C_6H_5^a$	C_6H_5	$COCH_3$	175	58	$C_{30}H_{20}O$	91.0	5.1	90.9	5.2
IXe	$C_6H_5^d$	C_6H_5	COOH	245–247	67	$C_{29}H_{16}O$	87.7	4.0	87.3	4.8
IXf	$C_6H_5^c$	C_6H_5	$COOCH_3$	180	61	$C_{30}H_{20}O_2$	87.4	4.9	87.3	5.2
IXg	$C_6H_5^b$	C_6H_5	$COOC_4H_9$	98	63	$C_{33}H_{26}O_2$	87.2	5.7	87.2	5.7
IXh	$C_6H_5^d$	C_6H_5	$CONH_2$	210	67	$C_{29}H_{19}NO$	87.6	4.8	87.8	5.0
IXi	$C_6H_5^a$	C_6H_5	$CONHC_3H_7$-i	250	64	$C_{32}H_{24}NO$	87.6	5.5	87.4	5.9
Xa**	$C_2H_5^g$	C_2H_5		320	94	$C_{26}H_{20}O_6$	72.8	4.7	72.5	4.8
Xb**	n-$C_6H_{13}^d$	n-C_6H_{13}		300–303	80	$C_{34}H_{36}O_6$	75.5	6.7	75.6	6.9
VIIa**	$C_2H_5^h$	C_2H_5		266	81	$C_{22}H_{16}O_3$	80.5	4.9	80.9	5.1
VIIb**	C_6H_5	C_6H_5		Ref. 5						
VIIc**	n-$C_6H_{13}^d$	n-C_6H_{13}		170	84	$C_{30}H_{32}O_3$	81.8	7.3	82.0	7.4
XI**	$C_2H_5^d$	C_2H_5		184	83	$C_{22}H_{18}O_3$	80.0	5.5	80.0	6.0

* All these compounds are white to pale yellow in color, except those marked**, which are bright yellow.

This behavior differs from that of acecyclone itself, which forms only a decarbonylated 1:1 adduct (5). As would be anticipated, acetylenedicarboxylic acid gives the completely aromatic anhydride (VII; R, R′ = C_6H_5) directly.



It is interesting to note the effects of substituents on the ultraviolet absorption characteristics of fluoranthene. Comparisons are made using the nomenclature of Jones (7). The solvent was dioxane unless otherwise indicated.

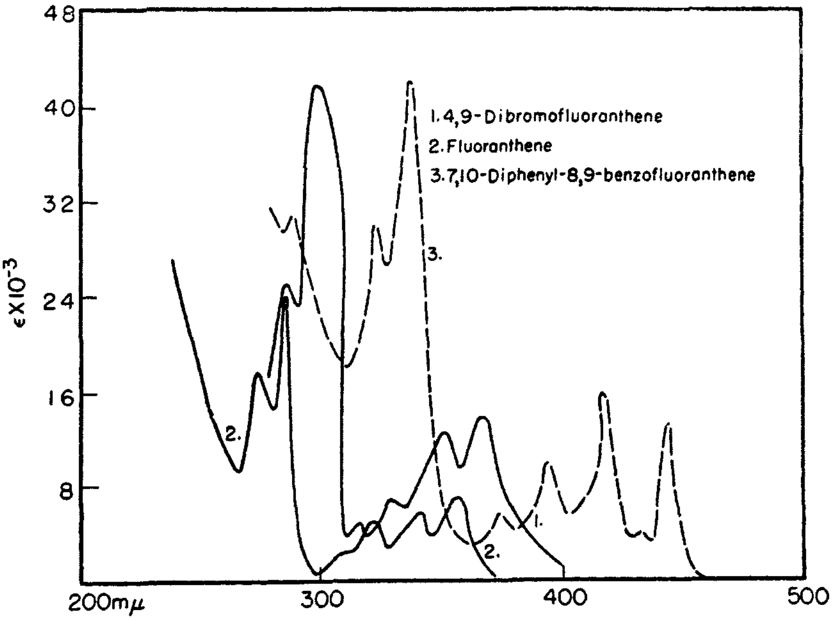


Fig. 1

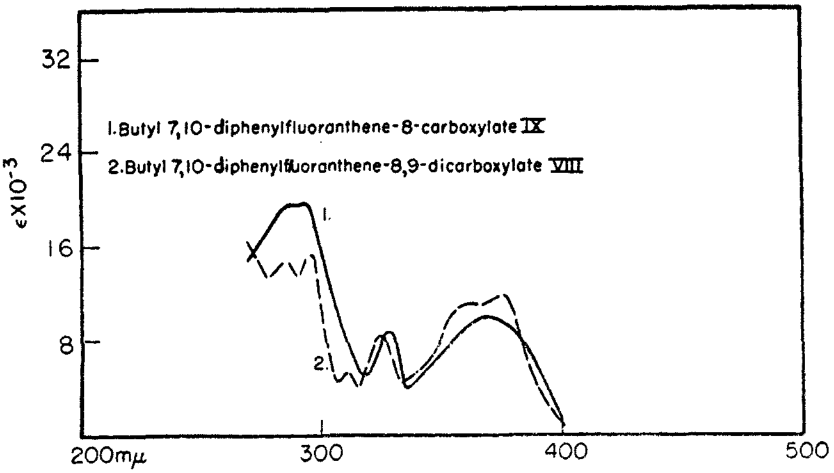


Fig. 2

A comparison of the ultraviolet spectra of fluoranthene and 4,9-dibromofluoranthene, which is included for comparison, shows a bathochromic shift due to the bromine, of about 120 Å units and a large increase in the molecular extinction coefficient (about double) (Fig. 1). The polynuclear compound, 7,10-

diphenyl-8,9-benzofluoranthene (7,14-diphenylacenaphth[1,2-*b*]anthracene), obtained from 1,4-dihydronaphthalene and acecyclone has an absorption spectrum, remarkable in the fact that it is almost identical with that of fluoranthene itself, but is shifted bathochromically about 800 Å. The bromine atoms have appreciably increased the resonance of the molecule, while retaining the fine structure.

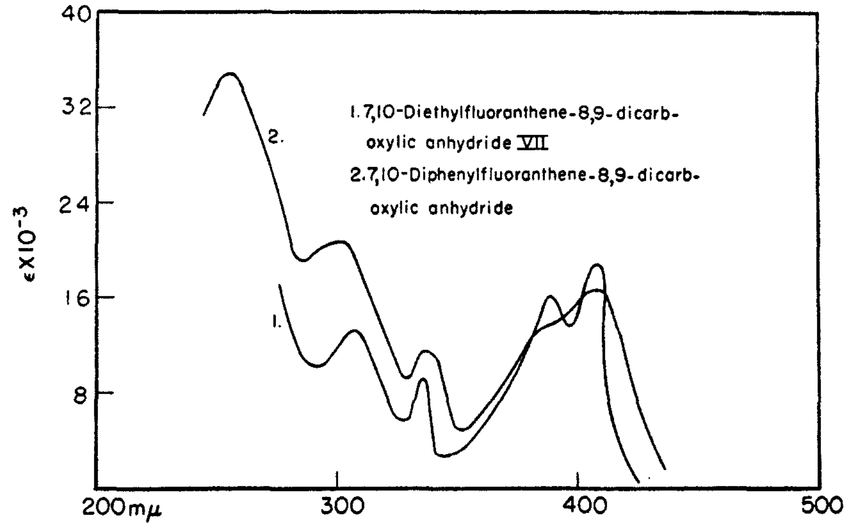


Fig.3

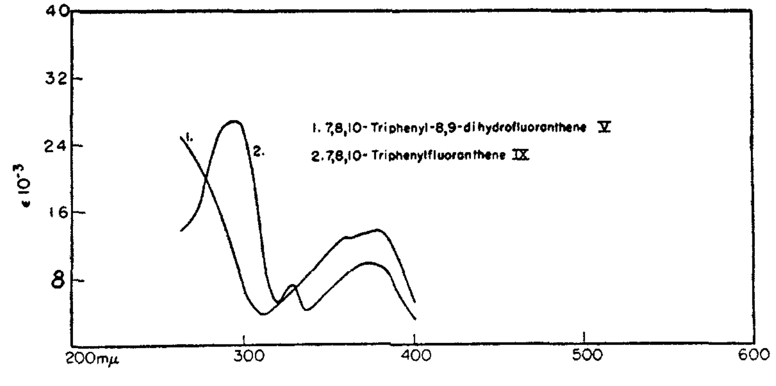


Fig.4

In Fig. 2, Curve 1 is the spectrum of butyl 7,10-diphenylfluoranthene-8-carboxylate (IXg). It is identical with the spectra of compounds IXd, IXe, IXf, and IXh, which are all monocarbonyl compounds, having the carbonyl substituents in the 8-position. The introduction of the carbonyl group leads to broadening of the absorption and loss of the fine structure typical of the conjugation effect. The absorption spectrum of butyl 7,10-diphenylfluoranthene-

8,9-dicarboxylate (VIIIg) (Fig. 2, Curve 2) is representative of the 8,9-dicarbonyl compounds; it is identical with the spectra of VIIIa, VIIIb, VIIIc, VIIIf, and VIIIg.

These compounds afford an interesting example of the conjugation effect (7) being partially suppressed by the steric effect. Although the carboxyl groups appear to be in conjugation with the aromatic ring system, the fine structure is largely retained. Only the B effect normal to a saturated substituent is observed. The planar 8,9-dicarboxylic acid anhydrides, Fig. 3, on the other hand, exhibit a typical C effect, broadening of the absorption, loss of fine structure, and a large bathochromic shift from 378 to 408 mμ. The anhydride grouping exerts considerably more interaction with the aromatic system, by virtue of its coplanarity, than do the other groups.

The curves for 7,8,10-triphenylfluoranthene and its 8,9-dihydro derivative are shown in Fib. 4. The dihydro derivative no longer has the fluoranthene absorption while the completely aromatic compound has an absorption almost identical with that of the monocarbonyl compounds shown in Fig. 2. The phenyl group appears to be equivalent to the carbonyl group as an auxochrome.

EXPERIMENTAL

The dienones (III). The carbinols (I) resulted when a mixture of 38 g. of acenaphthenequinone, 50 g. of a ketone (*i.e.*, diethyl), 300 ml. of methanol, and 50 ml. of a 20% methanolic potassium hydroxide solution were stirred at room temperature for three hours. The quinone dissolved, and subsequently the carbinol separated. The properties of some of the carbinols are collected in Table III. Since there was no need to isolate the carbinols, in some instances in which they did not crystallize readily the reaction mixture was poured into water, the precipitated oil was taken up in benzene or ether, dried, and the solvent removed. The residual oil was then dehydrated as described in the following procedure.

Dehydration was carried out by dissolving 13 g. of the carbinol in 15 g. of acetic anhydride and adding a drop of sulfuric acid. An immediate exothermic reaction took place, and the new substance crystallized. The new products were either dimers (II) (Table I) or dienones (III) (Table II).

It was later found that the dienone could be formed from the components without isolating the carbinols, the dehydration taking place when the alkaline solution was heated; in these cases, three hours' refluxing was employed.

An attempt to prepare a 2,4-dinitrophenylhydrazone of the carbinol (Ie) resulted in formation of the derivative of the corresponding cyclopentadienone.

Anal. Calc'd for $C_{27}H_{16}N_4O_4$: C, 70.5; H, 3.5.
Found: C, 70.2; H, 3.6.

The anhydrides (X, XI, XII). A solution of 3 g. of the dienone and 1.5 g. of maleic anhydride in 30 ml. of benzene was allowed to stand at room temperature for two days; a mass of yellow crystals separated. These were removed and recrystallized. They are the bridged anhydrides (XII); their properties are collected in Table VI.

When the solution was heated on the steam-bath, a vigorous reaction occurred at 70°; the vigorous reaction was over in five minutes, but the solution was refluxed for ten minutes more. After cooling, the anhydride (XI) was removed by filtration.

When equal weights of the components were refluxed in acetic acid solution for three hours, the bis-anhydrides (X) resulted.

The properties of these anhydrides are collected in Table VI.

Use of acetylenic addends. Esters of the dibasic acids (VIII) may be made with or without a solvent. For instance, equal weights of the dienone and an alkyl acetylenedicarboxylate were heated to 140°; carbon monoxide was evolved. The reaction was over in 20 minutes. When a solvent was employed; *e.g.*, *o*-dichlorobenzene, the solution was refluxed until the color had disappeared (about four hours), cooled to 100°, and added to twice its volume of petroleum ether. The addends used were methyl and butyl acetylenedicarboxylates, and propargyl alcohol.

The completely aromatic anhydride (VII) was most conveniently obtained by heating the dienone and acetylenedicarboxylic acid at 220–225° for three minutes.

Use of ethylenic addends. Equivalent amounts of dienone and ethylenic compound in three volumes of xylene were refluxed until the color had disappeared (about two hours). The solvent was then removed under reduced pressure, 1 g. of palladized charcoal was added, and the whole was heated for two hours at 250°/10 mm. The cooled residue was taken up in a solvent, filtered from the catalyst, and the fluoranthene (XI) crystallized. Alternatively, the dehydrogenation can be accomplished with permanganate and acetone (10).

TABLE VI

ENDOCARBONYLFLUORANTHENE ANHYDRIDES

NO.	R	R′	R″	R‴	M.P., °C.	YIELD, %	EMPIRICAL FORMULA	ANALYSES			
								Calc'd		Found	
								C	H	C	H
XIIa	C_2H_5[aa]	C_2H_5	—	—	162–164 dec.	88	$C_{23}H_{18}O_4$	77.0	5.0	76.7	5.2
XIIb	*n*-C_6H_{13}[bb]	*n*-C_6H_{15}	—	—	129–130 dec.	90	$C_{31}H_{34}O_4$	79.2	7.0	79.0	7.4

[aa] From methylene chloride-ligroin at room temperature.

[bb] From benzene-petroleum ether at room temperature.

If the dihydro compound (V) was desired, it was isolated by adding an equal volume of ligroin (90–120°) to the xylene solution of the reaction mixture. The properties of a few of these derivatives are collected in Table IV.

The addends used were styrene, *p*-chlorostyrene, 1,4-dihydronaphthalene, acrylic acid, methyl and butyl acrylates, acrylamide, N-isopropylacrylamide, and vinyl methyl ketone. *7,10-Diphenyl-8,9-benzofluoranthene*, formed in a 55% yield by the dehydrogenation of the adduct from 1,4-dihydronaphthalene and acecyclone, separated from benzene-acetic acid as deep brown crystals having a strong blue fluorescence; m.p. 250°.

Anal. Calc'd for $C_{36}H_{22}$: C, 95.2; H, 4.8.

Found: C, 94.9; H, 4.6.

The properties of the fluoranthene derivatives are collected in Table V.

SUMMARY

A large number of substituted fluoranthenes have been prepared. The preferred method of synthesis consists in the condensation of acenaphthenequinone with a ketone having two *alpha*-methylene groups to give an acecyclone. The latter, with ethylenic addends, gives endocarbonyl fluoranthenes, which are readily decarbonylated and dehydrogenated to yield the fluoranthenes. The latter are also obtained directly by the use of acetylenic addends.

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