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E. JOSEPHY AND F. RADT

Volume 14

TETRACYCLIC AND HIGHER-CYCLIC COMPOUNDS

Series III

CARBOISOCYCLIC CONDENSED COMPOUNDS

ELSEVIER PUBLISHING COMPANY, INC.
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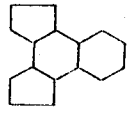
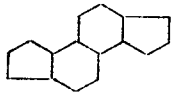
III. Tetracyclic Compounds

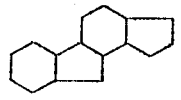
SUMMARY OF THE RING SYSTEMS*



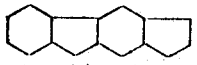
[1.2; 3.4-Dicyclopentenonaphthalene], p. 4.



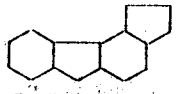
p. 5.



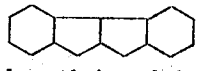
1.2-Cyclopentenofluorene, p. 5.



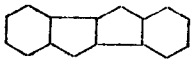
[2.3-Cyclopentenofluorene], p. 6.



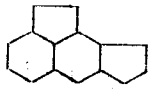
[3.4-Cyclopentenofluorene], p. 6.



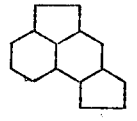
[Indeno-2′.3′: 2.3-indene], p. 6.



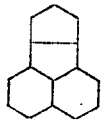
Diphensuccindene, p. 6.



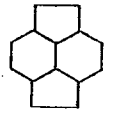
[3.4-Cyclopentenoacenaphthene], p. 11.



[4.5-Cyclopentenoacenaphthene], p. 11.



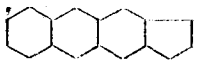
Acecyclone, p. 11.



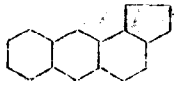
[5.6-Ace-acenaphthene], p. 12.

* Under the formula skeletons is quoted an important representative, usually the parent hydrocarbon, and the page where the system begins; on this page the numbering is to be found. If no simple compounds of the given system are known the name of a hypothetic parent hydrocarbon generally is quoted in brackets.

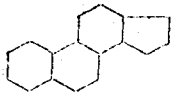
3. Compounds with 1 Five- and 3 Six-Membered Rings p. 12



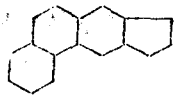
2.3-Cyclopenteno-anthracene, p. 12.



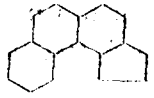
1.2-Cyclopenteno-anthracene, p. 12.



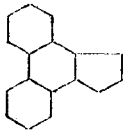
1.2-Cyclopenteno-phenanthrene, p. 13.



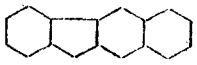
2.3-Cyclopenteno-phenanthrene, p. 289.



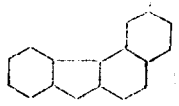
3.4-Cyclopenteno-phenanthrene, p. 290.



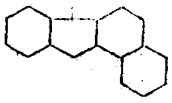
9.10-Cyclopenteno-phenanthrene, p. 291.



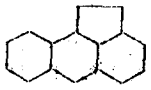
2.3-Benzfluorene, p. 295.



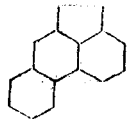
3.4-Benzfluorene, p. 297.



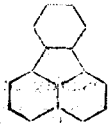
1.2-Benzfluorene, p. 299.



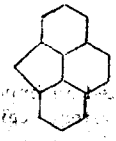
Aceanthrene, p. 302.



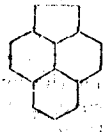
Acephenanthrene, p. 304.



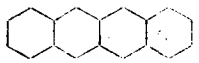
Fluoranthene, p. 305.



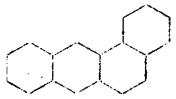
4.5-Methylene-phenanthrene, p. 309.



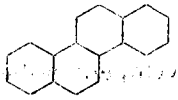
[5.6-Trimethylene-acenaphthene], p. 310.



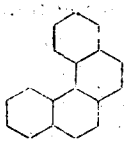
Naphthacene, p. 311.



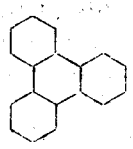
1.2-Benzanthracene, p. 329.



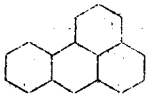
Chrysene, p. 343.



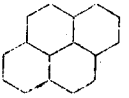
3.4-Benzphenanthrene, p. 356.



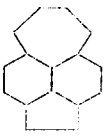
Triphenylene, p. 357.



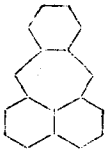
Benzanthrene, p. 358.



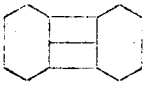
Pyrene, p. 376.



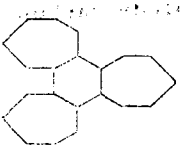
p. 396.



Pleiadene, p. 396.



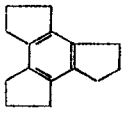
p. 399.



p. 399.

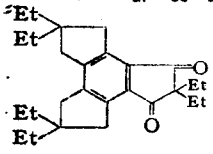
1. Tetracyclic Compounds with 3 Five-Membered Rings and 1 Six-Membered Ring

Tricyclopentenobenzene $C_{15}H_{18}$. Needles (alc.), m. 97° (1925 Perkin). — **Fmn.**



From cyclopentanone satd. with HCl on standing (1897 Wallach). From cyclopentylideneazine in tetralin with dry HCl at 180° (1925 Perkin). From 1.2-dibromocyclopentene with Na in ether (1936 Favorsky).

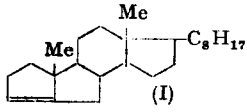
Compd. $C_{27}H_{38}O_2$, probably **2.2-diethyl-4.5;6.7-bis-(4.4-diethylcyclopenteno)-indan-1.3-dione.**



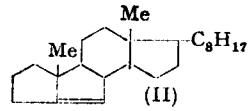
Scales (dil. alc.), m. 62–3°. — **Fmn.** 2.2-Diethylindan + diethylmalonyl chloride $\xrightarrow{AlCl_3 \text{ in } CS_2}$ a condens. product, which is reduced and then condensed with more diethylmalonyl chloride. — **Rns.** With HNO_3 at 140–50° → mellitic acid (1918 Freund).

1897 Wallach, *Ber.* **30** 1094. **1918** Freund, Fleischer, *Ann.* **414** 1.
1925 Perkin, Plant, *J. Ch. Soc.* **127** 1138.
1936 Favorsky, *J. Gen. Ch. U.S.S.R.* **6** 720; *Bull. soc. chim.* [5] **3** 1727.

Hydrocarbon $C_{25}H_{42}$, (I) or (II), see p. 20.



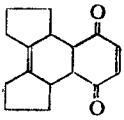
(I)



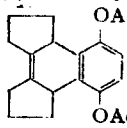
(II)

2. Tetracyclic Compounds with 2 Five- and 2 Six-Membered Rings

1.2;3.4-Dicyclopenteno-1.4.9.10-tetrahydro-5.8-naphthoquinone, $C_{16}H_{18}O_2$, (I). Pale yellow cryst. (toluene), m. 124°. — **Fmn.** From $\Delta^{1.1'}$-bicyclopentenyl + benzoquinone on boiling in MeOH. — **Rns.** With Ac_2O and pyr. on boiling → **diacetate** $C_{20}H_{22}O_4$, (II), m. 145°. With $\Delta^{1.1'}$-bicyclopentenyl on boiling → octahydrotetracyclopenteno-anthraquinone (p. 497). Condenses similarly with octahydrobiphenyl (1935 Barnett).

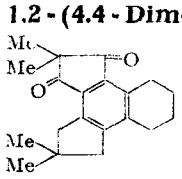


(I)



(II)

1.2-(4.4-Dimethylcyclopenteno)-3.4-dimethylmalonyl-5.6.7.8-tetrahydronaphthalene $C_{20}H_{24}O_2$, m. 148–9°. — **Fmn.** From 2.2-dimethyl-4.5-cyclohexenoindan and dimethylmalonyl chloride. — **Rns.** With Zn,Hg in HCl → the corresp. **hydrocarbon** $C_{20}H_{28}$ [m. 105–6°]. With fuming HNO_3 in a bomb → 2.2-dimethylindan-1.3-dione-4.5.6.7-tetracarboxylic acid and mellitic acid. With aq. KOH → an **acid** $C_{20}H_{26}O_3$ [m. 181°; no rn. with phenylhydrazine] (1920, 1921 Fleischer).



1920 Fleischer, Siefert, *Ber.* **53** 1255. 1921 Fleischer, Siefert, *Ann.* **422** 272.
1935 Barnett, Lawrence, *J. Ch. Soc.* **1935** 1104.

Hydrocarbon $C_{26}H_{44}$, (I), see p. 64.

Hydrocarbon $C_{26}H_{46}$, (II), see p. 64.

Ketones $C_{26}H_{44}O$, (III), (IV), and homologues, see pp. 63, 64, 84.

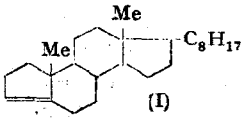
Desoxypyrolithobilianic acid $C_{23}H_{38}O_2$, (V), see p. 215.

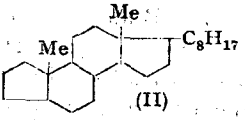
Pyrolithobilianic acid $C_{23}H_{36}O_3$, (VI), see p. 215.

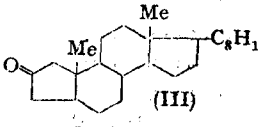
Pyroisolithobilianic acid $C_{23}H_{36}O_3$, (VII), see p. 215.

Pyrodesoxybilianic acid $C_{23}H_{34}O_4$, (VIII), see p. 218.

Pyroisodesoxybilianic acid $C_{23}H_{34}O_4$, (IX), see p. 220.


(I)


(II)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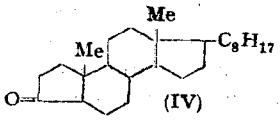
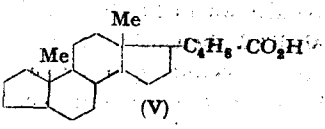

(IV)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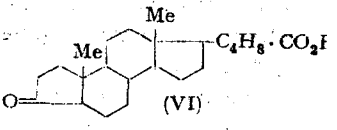
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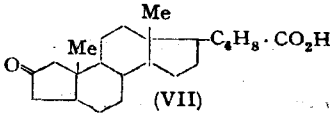
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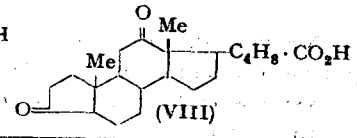
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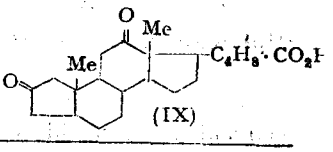
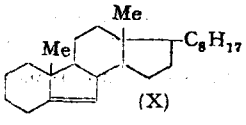
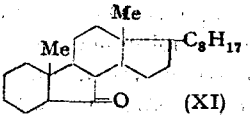
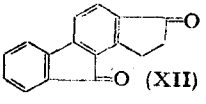

(IX)

Hydrocarbon $C_{26}H_{44}$, (X), see p. 20.


(X)

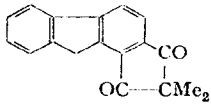
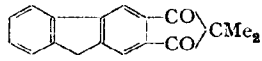
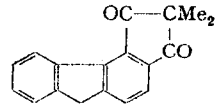

(XI)


(XII)

Ketone $C_{26}H_{44}O$, (XI), see p. 64.

3'-Keto-1.2-cyclopentenofluorenone $C_{16}H_{10}O_2$, (XII). Dark yellow cryst. (acet. ac.), m. 236°. — **Fmn.** From β-(1-fluorenonyl)-propionic acid chloride with $AlCl_3$ in CS_2 (1932 v. Braun, Manz, *Ann.* **496** 170).

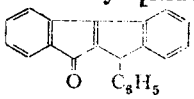
Dimethylmalonylfluorenes $C_{18}H_{14}O_2$. Two compds., m. 220–1°, 156–8°, resp.,

having two of the above constitutions are formed from fluorene and dimethylmalonyl chloride with $AlCl_3$. They are oxid. by $Na_2Cr_2O_7$ in acet. ac. to the corresp. **fluorenones** $C_{18}H_{12}O_3$, both melting at 263° but giving a strong m.p. depression, and reduced by Clemmensen's method to the corresp. **hydrocarbons** $C_{18}H_{18}$, m. 128–9°, 135–7°, resp.

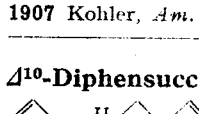
1918 Freund, Fleischer, *Ann.* **414** 1, 47.

1'-Phenyl-[indeno-2'.3':2.3-indone] $C_{22}H_{14}O$. Yellow plates (alc.), m. 162°; with H_2SO_4 red, then dark green soln. — **Fmn.** From 2-benzalindandione with C_6H_5MgBr in boil. benz.-ether. — **Rns.** With $KMnO_4$ in acetone → 2-o-carboxybenzoyl-diphenylacetic acid.

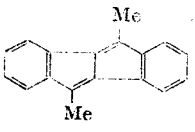


1907 Kohler, *Am. Ch. J.* **37** 369.

Δ^{10}-Diphensuccindene $C_{16}H_{12}$. For name and numbering see 1922 Brand. Slightly yellowish leaflets (alc.), m. 210°; fairly sol. in ordinary org. solvents, in H_2SO_4 green, but the alc. soln. on addn. of H_2SO_4 turns red (1922 Brand). — **Fmn.** From 9.12-dichloro-$\Delta^{9.11}$-diphensuccindadiene with Zn (+ a few drops of $HgCl_2$ soln.) in alc. on refluxing, or with Zn in $C_5H_{11}OH$ or acet. ac. (1922 Br.). By Zn-$HgCl_2$ redn. of 12-chloro-9-methoxy-$\Delta^{9.11}$-diphensuccindadiene or the corresp. ethoxy compd. in acet. ac. (1926 Br.). — **Rns.** With H_2, Pd-charcoal in warm dil. alc. → diphensuccindan. With benzaldehyde (Na in alc.) → **9-benzal-Δ^{10}-diphensuccindene** $C_{23}H_{16}$ [brown-red cryst., m. 155°] and 9.12-dibenzal-Δ^{10}-diphensuccindene (1922 Br.). With p-nitrosodimethylaniline in absol. alc. at 50–60° → bis-(p-dimethylaminoanil) of Δ^{10}-diphensuccindene-9.12-dione (1936 a Br.).



Diphensuccindan $C_{16}H_{14}$. Needles (dil. alc.), m. 102° (1922 Brand). — **Fmn.** From diphensuccindandione with HI (b. 127°) and red P at 170–80° (1888 Roser). From Δ^{10}-diphensuccindene with H_2, Pd-charcoal in warm dil. alc. (1922 Br.).



9.12-Dimethyl-$\Delta^{9.11}$-diphensuccindadiene $C_{18}H_{14}$. Deep red (amyl acetate), brown-red (acet. ac.), yellow-brown (alc.), needles, m. 212°, the powdered compd. is yellow. — **Fmn.** From 9.12-dimethyldiphensuccindan-9.12-diol in acet. ac. with formic acid. — **Rns.** With H_2, Pd-charcoal in warm dil. alc. → **9.12-dimethyldiphensuccindan** $C_{18}H_{18}$ [needles, m. 94°] (1923 a Brand).

9.12-Diethyl-$\Delta^{9.11}$-diphensuccindadiene $C_{20}H_{18}$. Red to red-brown leaflets (MeOH), m. ca. 154°. — **Fmn.** On boiling 9.12-diethylsuccindan-9.12-diol with a large excess of formic acid in acet. ac. (10 hrs.) (1923 a Brand).

9.12-Dipropyl-$\Delta^{9.11}$-diphensuccindadiene $C_{22}H_{22}$. Red needles (alc.), m. 135–136°. — **Fmn.** From 9.12-dipropyldiphensuccindan-9.12-diol with formic acid in

acet. ac. — **Rns.** With H_2, Pd-charcoal in dil. alc. → 9.12-dipropyldiphensuccindan (1925 f Brand).

9.12-Dipropyldiphensuccindan $C_{22}H_{26}$. Needles (alc.), m. 98–9°. — **Fmn.** From the foregoing compd. or 9.12-dipropylidenediphensuccindan, q.v. (1925 f Brand).

9.12-Diisopropyl-$\Delta^{9.11}$-diphensuccindadiene $C_{22}H_{22}$. Red cryst. (alc.), m. 178–9°. — **Fmn.** From 9.12-diisopropyldiphensuccindan-9.12-diol with formic acid in acet. ac. — **Rns.** With H_2 and Pd-charcoal in dil. alc. → **9.12-diisopropyldiphensuccindan** $C_{22}H_{26}$ [needles, m. 80–1°] (1925 f Brand).

9.12-Diphenyl-$\Delta^{9.11}$-diphensuccindadiene $C_{28}H_{18}$. Brown. crystals (AcOEt), m. 259–60°; strongly electrified on rubbing (1912 Brand). — **Fmn.** From 9.12-diphenyldiphensuccindan-9.12-diol with formic acid in acet. ac. (1912 Br.). — **Rns.** With CrO_3 in boiling acet. ac. → o-benzoylbenzoic acid; with CrO_3 in cold acet. ac. → o.o'-dibenzoylbenzil (1930 a Br.). Redn. with Zn dust in acet. ac. → 9.12-diphenyl-Δ^{10}-diphensuccindene (1925 c Br.). With Na in $C_5H_{11}OH$ → 9.12-diphenyldiphensuccindan (two stereoisomerides); with H_2 and Pd-charcoal in warm acet. ac. → the form, m. 207–8° (1925 c Brand).

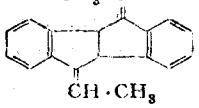
9.12-Diphenyl-Δ^{10}-diphensuccindene $C_{28}H_{20}$. Needles (acet. ac.), m. 285–6°, the $CHCl_3$ soln. fluoresces strongly. — **Fmn.** From 9.12-diphenyldiphensuccindadiene with Zn dust in acet. ac. — **Rns.** With CrO_3 in acet. ac. → o-benzoylbenzoic acid and o.o'-dibenzoylbenzil. With H_2, Pd-charcoal in warm acet. ac. → 9.12-diphenyldiphensuccindan, m. 207–8°. With 1 mol. of Br_2 in CS_2 → 9.12-diphenyl-$\Delta^{9.11}$-diphensuccindadiene (1925 c Brand).

9.12-Diphenyldiphensuccindan $C_{28}H_{22}$. Two stereoisomeric forms, needles (AcOEt), m. 207–8° and 166–7°, resp., both exhibit fluorescence in $CHCl_3$ soln. — — **Fmn.** From 9.12-diphenyl-$\Delta^{9.11}$-diphensuccindadiene with Na in $C_5H_{11}OH$. The form, m. 207–8°, is also made from 9.12-diphenyl-$\Delta^{9.11}$-diphensuccindadiene or diphenyl-Δ^{10}-diphensuccindene in warm acet. ac. with H_2 and Pd-charcoal (1925 c Brand).

Aryl	Other Derivatives of								
	$\Delta^{9.11}$-Diphensuccindadiene			Δ^{10}-Diphensuccindene			Diphensuccindan		
	Formula	M.p.	Ref.	Formula	M.p.	Ref.	Formula	M.p.	Ref.
9.12-Di-o-tolyl-	$C_{30}H_{22}$	240°	(7)	—	—	—	—	—	—
9.12-Di-m-tolyl-	$C_{30}H_{22}$	184–5°	(7)	$C_{30}H_{24}$	179–80°	(5)	$C_{30}H_{26}$	150°	(5)
9.12-Di-p-tolyl-	$C_{30}H_{22}$	271–2°	(1)	$C_{30}H_{24}$	200°	(5)	$C_{30}H_{26}$	188-9°, 145–6°	(5)
9.12-Dibenzyl-	—	—	—	—	—	—	$C_{30}H_{26}$	141°	(3)
9.12-Bis-3.4-dimethylphenyl-	$C_{32}H_{26}$	212°	(7)	—	—	—	—	—	—
9.12-Bis-o-methoxyphenyl-	$C_{30}H_{22}O_2$	247°	(2)	$C_{30}H_{24}O_2$	254–5°	(6)	$C_{30}H_{26}O_2$	250–1°	(6)
9.12-Bis-p-methoxyphenyl-	$C_{30}H_{22}O_2$	242°	(2)	—	—	—	$C_{30}H_{26}O_2$	244–5°	(6)
9.12-Bis-o-ethoxyphenyl-	$C_{32}H_{26}O_2$	204–5°	(6)	$C_{32}H_{28}O_2$	250°	(6)	$C_{32}H_{30}O_2$	175–6°	(6)
9.12-Bis-p-ethoxyphenyl-	$C_{32}H_{26}O_2$	223–4°	(6)	$C_{32}H_{28}O_2$	250–1°	(6)	$C_{32}H_{30}O_2$	240–1°	(6)
9.12-Di-β-naphthyl-	$C_{36}H_{22}$	266°	(4)	—	—	—	$C_{36}H_{26}$	225°	(4)

(1) 1912 Brand (2) 1920 b Brand (3) 1922 Brand (4) 1923 b Brand (5) 1925 c Brand (6) 1925 d Brand (7) 1925 e Brand.

9.12-Diethylidenediphensuccindan $C_{20}H_{18}$. Needles (alc., AcOEt), m. 199.5°; difficultly sol. in most solvents. — **Fmn.** On refluxing 9.12-diethyldiphensuccindan-9.12-diol with formic acid in acet. ac. (1 hr.). — **Rns.** With CrO_3 in warm acet. ac. → diphensuccindandione and acetaldehyde (1923 a Brand).



9.12-Dipropylidenediphensuccindan $C_{22}H_{22}$. Needles (alc.), m. 157–8°. — **Fmn.** From 9.12-dipropyldiphensuccindan-9.12-diol with formic acid in acet. ac. — **Rns.** With CrO_3/H_2SO_4 → diphensuccindandione and propionaldehyde. With H_2 and Pd-charcoal in dil. alc. → 9.12-dipropyldiphensuccindan (1925 f Brand).

9.12-Diisopropylidenediphensuccindan $C_{22}H_{22}$. Needles, m. 189°. — **Fmn.** From 9.12-diisopropyldiphensuccindan-9.12-diol with formic acid in acet. ac. or better with HCl in alc. — **Rns.** With CrO_3/H_2SO_4 → diphensuccindandione and acetone (1925 f Brand).

9.12-Dibenzal-Δ^{10}-diphensuccindene $C_{30}H_{20}$. Cinnabar-red leaflets (amyl acetate), m. 244°. — **Fmn.** From Δ^{10}-diphensuccindene or 9-benzal-Δ^{10}-diphensuccindene with benzaldehyde (Na in alc.). — **Rns.** With H_2, Pd-charcoal in warm alc.-acet. ac. → 9.12-dibenzyldiphensuccindan. On boiling with Zn dust in acet. ac. → 9.12-dibenzaldiphensuccindan (1922 Brand).

9.12-Dibenzaldiphensuccindan $C_{30}H_{22}$. Needles (amyl acetate), m. 255° (1922 Brand). — **Fmn.** From 9.12-dibenzal-Δ^{10}-diphensuccindene on boiling with Zn dust in acet. ac. (1922 Brand). From 9.12-dibenzyldiphensuccindan-9.12-diol in boiling acet. ac. with formic acid (1923 a Brand). — **Rns.** With CrO_3 in acet. ac. → diphensuccindan-9.12-dione and benzoic acid (1923 a Brand). With H_2, Pd-charcoal in warm alc.-acet. ac. → 9.12-dibenzyldiphensuccindan (1922 Brand).

9.12-Dichloro-$\Delta^{9.11}$-diphensuccindadiene $C_{16}H_8Cl_2$. Red-brown needles (alc.), m. 191° (1922 Brand). — **Fmn.** From 9.9.12.12-tetrachlorodiphensuccindan with NaOAc in alc. or on standing in benzene soln. (1922 Brand). — **Rns.** With $Zn/HgCl_2$ in boiling alc. or with Zn/amyl alc. or acet. ac. → Δ^{10}-diphensuccindene (1922 Brand). The toluene soln. with NaOMe on refluxing → 12-chloro-9-methoxy-$\Delta^{9.11}$-diphensuccindadiene (1926 Brand).

9.9.12.12-Tetrachlorodiphensuccindan $C_{16}H_{10}Cl_4$. Needles (benzene), m. 135° dec. — **Fmn.** From diphensuccindandione on heating with PCl_5. — **Rns.** Readily loses HCl → 9.12-dichloro-$\Delta^{9.11}$-diphensuccindadiene (1922 Brand).

12-Chloro-9-methoxy-$\Delta^{9.11}$-diphensuccindadiene $C_{17}H_{11}OCl$. Dark red leaflets (alc. or acet. ac.), m. 178.5°. — **Fmn.** From 9.12-dichloro-$\Delta^{9.11}$-diphensuccindadiene, q.v. — **Rns.** With $Zn/HgCl_2$ in boiling acet. ac. → Δ^{10}-diphensuccindene (1926 Brand).

12-Chloro-9-ethoxy-$\Delta^{9.11}$-diphensuccindadiene $C_{18}H_{13}OCl$. Brown-red needles, m. 123° (1926 Brand).

9.12-Dimethyldiphensuccindan-9.12-diol $C_{18}H_{18}O_2$. Needles (alc.), m. 170° dec.; sol. in most org. solvents. — **Fmn.** From diphensuccindan-9.12-dione with

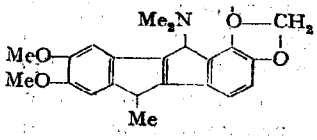
CH_3MgI. — **Rns.** With formic acid in acet. ac. → 9.12-dimethyl-$\Delta^{9.11}$-diphensuccindadiene (1923 a Brand).

9.12-Diethyldiphensuccindan-9.12-diol $C_{20}H_{22}O_2$. Cryst. (ligroin), m. 102°. — **Fmn.** From diphensuccindan-9.12-dione with C_2H_5MgBr. — **Rns.** With formic acid in acet. ac. → 9.12-diethylidenediphensuccindan and 9.12-diethyl-$\Delta^{9.11}$-diphensuccindadiene (1923 a Brand).

Other Derivatives of Diphensuccindan-9.12-diol

9.12-Dipropyl-	$C_{22}H_{26}O_2$	m. 121–2°	1925 f Brand
9.12-Diisopropyl-	$C_{22}H_{26}O_2$	,, 132–3°	1925 f ,,
9.12-Diphenyl-	$C_{28}H_{22}O_2$	,, 232–4° dec.	1912 ,,
9.12-Di-m-tolyl-	$C_{30}H_{26}O_2$	,, 180°	1925 e ,,
9.12-Di-p-tolyl-	$C_{30}H_{26}O_2$	,, 248–50° dec.	1912 ,,
9.12-Dibenzyl-	$C_{30}H_{26}O_2$	,, 206°	1926 a ,,
9.12-Bis-3.4-dimethylphenyl-	$C_{32}H_{30}O_2$	,, 252°	1925 e ,,
9.12-Bis-o-methoxyphenyl-	$C_{30}H_{26}O_4$	,, 207.5°	1920 b ,,
9.12-Bis-p-methoxyphenyl-	$C_{30}H_{26}O_4$	,, 230°	1920 b ,,
9.12-Bis-o-ethoxyphenyl-	$C_{32}H_{30}O_4$	,, 213–5°	1925 d ,,
9.12-Bis-p-ethoxyphenyl-	$C_{32}H_{30}O_4$	,, 208°	1925 d ,,
9.12-Di-β-naphthyl-	$C_{36}H_{26}O_2$	,, 286–7°	1923 b ,,

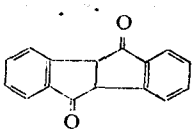
Compd. $C_{22}H_{23}O_4N$, possibly **9-methyl-12-dimethylamino-3.4-methylenedioxy-6.7-dimethoxy-Δ^{10}-diphensuccindene.**



Pale ochreous, m. about 100°; forms yellow solns. in alc. and benzene. — **Fmn.** By boiling isoanhydrokryptopine methosulphate with dil. NaOH (1916 Perkin).

Δ^{10}-Diphensuccindene-9.12-dione $C_{16}H_8O_2$. — **Fmn.** The bis-p-dimethylaminoanil is formed from Δ^{10}-diphensuccindene and p-nitrosodimethylaniline with Na in absol. alc. at 50–60°. — **Rns.** From the above mentioned dianil with HCl in benzene, alc. or water the free dione is not obtained, but a **compd.** $C_{31}H_{16}O_3$ [red cryst., m. 284°; resistant towards SO_2; no oxime, no phenylhydrazone] + CO; the dioxime in boiling acet. ac. with $NaNO_2$ gives the same product. — *Bis-p-dimethylaminoanil* $C_{32}H_{28}N_4$, dark violet cryst., m. 274–77.5°, according to the rate of heating. — *Dioxime* $C_{16}H_{10}O_2N_2$, violet-red, m. 272° (1936 a Brand).

Diphensuccindan-9.12-dione and/or the enolic form $C_{16}H_{10}O_2$. Prisms (alc.), m. 202°, insol. in water (1881 Reimer), the soln. in NaOH is orange (1912 Brand). — **Fmn.** From the α.α'-diphenylsuccinic acids (better from the form with the higher m. pt.), with H_2SO_4 at 130° (1881 Reimer; 1888 Roser). — **Rns.** With HI (b. 127°) and P at 170–80° → diphensuccindan (1888 Roser). With SeO_2 in boiling acet. ac. → red compd. $C_{31}H_{16}O_3$, m. 284° (see Δ^{10}-diphensuccindene-9.12-dione) (1936 a Brand). With boiling HNO_3 (d 1.4) → benzil-o.o'-dicarboxylic acid and a **compd.** $C_{16}H_8O_6$ or $C_{32}H_{14}O_{12}$ [m. 236°]; with boiling $HNO_3 + V_2O_5$ → phthalic acid, benzil-o.o'-dicarboxylic acid and the compd. m. 236° (above) (1925 a Brand). With KNO_3/H_2SO_4 → 2.6-dinitro-deriv. (1925 b Brand). With dil.



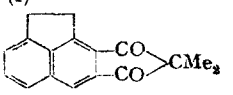
$KMnO_4$ → benzil-o.o'-dicarboxylic acid (1925 a Brand). With Br_2 in boiling CCl_4 exposed to light from an arc-lamp → 10-bromodiphensuccindan-9.12-dione (1936 a Brand). On warming with PCl_5 → 9.9.12.12-tetrachlorodiphensuccindan (1922 Brand). With conc. NaOH on warming changes partly into an isomeric or polymeric insol. form, m. 280–90° (1888 Roser). Reacts with alkyl and aryl Grignard reagents to give the expected diols (1912, 1920 b, 1923 a, b, 1925 d, e, f Brand). — *Dioxime* $C_{16}H_{12}O_2N_2$, m. 254°dec. (1888 Roser). — *Bis-phenylhydrazone* $C_{28}H_{22}N_4$, yellow needles, m. 260–70°dec. (1888 Roser).

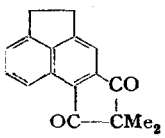
10-Bromodiphensuccindan-9.12-dione $C_{16}H_9O_2Br$. Leaflets (MeOH with a trace of HCl), m. 147°; solubilities: 8 g./100 c.c. in boiling MeOH, 50 g./100 c.c. in boiling benzene; insol. in petrol. ether of b. pt. ca. 50°(1936 a Brand). — **Fmn.** From diphensuccindan-9.12-dione with Br_2 in boiling CCl_4 exposed to light from an arc-lamp (1936 a Brand). — **Rns.** On heating to 200–50° → HBr and red compd. $C_{31}H_{16}O_3$ (see Δ^{10}-diphensuccindene-9.12-dione, p. 9), the same prod., together with CO, is formed with fused NaOAc in boiling alc. With Zn dust/$HgCl_2$ in alc. or with H_2 and ZnO-Pd in dil. alc. → diphensuccindan-9.12-dione (1936 a Brand). The boiling alc. solution gives with pyr. the compd. $C_{31}H_{16}O_3$ (above), with piperidine small amts. of the same compd. and a compd. m. 166.5°. On slow addn. of cyclohexylamine in alc. to the dione in boiling alc. the red compd. $C_{31}H_{16}O_3$ is formed, on rapid addn. the product is **10-cyclohexylaminodiphensuccindan-9.12-dione** $C_{22}H_{21}O_2N$, m. 141° (1936 b Brand). The following amino-compds. are prepd. in a similar way: **10-anilinodiphensuccindan-9.12-dione** $C_{22}H_{15}O_2N$, m. 202.5°; **10-o-toluidinodiphensuccindan-9.12-dione** $C_{23}H_{17}O_2N$, m. 167.5°; **10-m-toluidinodiphensuccindan-9.12-dione** $C_{23}H_{17}O_2N$, m. 191.5°; **10-p-toluidinodiphensuccindan-9.12-dione** $C_{23}H_{17}O_2N$, m. 180.5°; **10-(2-methoxyanilino)-diphensuccindan-9.12-dione** $C_{23}H_{17}O_3N$, m. 169°; **10-(3-methoxyanilino)-diphensuccindan-9.12-dione** $C_{23}H_{17}O_3N$, m. 187°; **10-(4-methoxyanilino)-diphensuccindan-9.12-dione** $C_{23}H_{17}O_3N$, m. 145.5°; **10-(2-ethoxyanilino)-diphensuccindan-9.12-dione** $C_{24}H_{19}O_2N$, m. 179°; **10-(3-ethoxyanilino)-diphensuccindan-9.12-dione** $C_{24}H_{19}O_3N$, m. 175.5°; **10-(4-ethoxyanilino)-diphensuccindan-9.12-dione** $C_{24}H_{19}O_3N$, m. 135°; **10-β-naphthylaminodiphensuccindan-9.12-dione** $C_{26}H_{17}O_2N$, m. 173°; all these arylamino compds. except the 3-methoxy- and 3-ethoxy-derivs. give with conc. H_3PO_4 in acet. ac. the red compd. $C_{31}H_{16}O_3$ (1936 b Brand).

2.6-Dinitrodiphensuccindan-9.12-dione $C_{16}H_8O_6N_2$. Needles, m. 241° or yellow prisms, m. 244°. — **Fmn.** From diphensuccindandione with KNO_3/H_2SO_4. — **Rns.** On boiling with dil. $KMnO_4$-$MgSO_4$ soln. → 4-nitrophthalic acid. Sn and HCl red. the nitro groups (1925 b Brand).

1881 Reimer, *Ber.* **14** 1802. **1888** Roser, *Ann.* **247** 152.
1912 Brand, *Ber.* **45** 3071. **1916** Perkin, *J. Ch. Soc.* **109** 815, 864, 1006.
1920 a Brand, Ludwig, *Ber.* **53** 809. — b Brand, Hoffmann, *Ber.* **53** 815.
1922 Brand, Müller, *Ber.* **55** 601.
1923 a Brand, Schläger, *Ber.* **56** 2541. — b Brand, Trebing, *Ber.* **56** 2545.
1925 a Brand, Loehr, *J. pr. Ch.* [2] **109** 353. — b Brand, Loehr, *J. pr. Ch.* [2] **109** 359. — c Brand, Mühl, *J. pr. Ch.* [2] **110** 1. — d Brand, Krey, *J. pr. Ch.* [2] **110** 10. — e Brand, Ludwig, Berlin, *J. pr. Ch.* [2] **110** 26. — f Brand, Sasaki, *Ber.* **58** 2546.
1926 Brand, Müller, Kessler, *Ber.* **59** 1962.
1936 a Brand, Gabel, Ott, *Ber.* **69** 2504. — b Brand, Ott, *Ber.* **69** 2514.

3.4 (or 4.5)-Dimethylmalonylacenaphthene $C_{17}H_{14}O_2$, (I) or (II), resp. Light yellow needles (alc.), m. 176.5–177.5°; sol. in org. solvents, the soln. in H_2SO_4 is red-yellow. — **Fmn.** In small amt. from acenaphthene + dimethylmalonyl chloride with $AlCl_3$ in CS_2. — **Rns.** Cleavage on boiling with conc. KOH (1913 Freund).

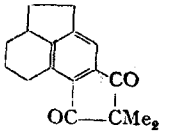
(I) 

(II) 

3.4 (or 4.5)-Diethylmalonylacenaphthene $C_{19}H_{18}O_2$. Light yellow powder (MeOH), m. 109–111°, red coloration with H_2SO_4 (1910, 1914 Freund). — **Fmn.** In small amt. from acenaphthene + diethylmalonyl chloride with $AlCl_3$ in CS_2. — **Rns.** On boiling with KOH soln. → a diethylacetylacenaphthenecarboxylic acid, m. 168–70°dec. (1914 Freund).

For two **dipropylmalonylacenaphthenes** $C_{21}H_{22}O_2$, m. 154–154.5° and 126°, resp., both formed from acenaphthene + dipropylmalonyl chloride with $AlCl_3$ in CS_2, possibly belonging to one of the systems represented by (I) and (II), see 1913 Freund.

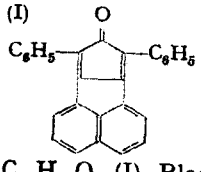
4.5 - Dimethylmalonyl - 6.7.8.9 - tetrahydroacenaphthene $C_{17}H_{18}O_2$. Cryst. (MeOH), m. 105–6°. — **Fmn.** From tetrahydroacenaphthene and dimethylmalonyl chloride + $AlCl_3$. — **Rns.** With Zn,Hg in HCl→ the corresp. **hydrocarbon** $C_{17}H_{22}$ [b. 173–5°/$_{13}$, d^{22} 0.9884, n_D 1.5399]. With fuming HNO_3 in a bomb at 160° → 2.2-dimethylindan-1.3-dione-4.5.6-tricarboxylic acid (1921 Fleischer).

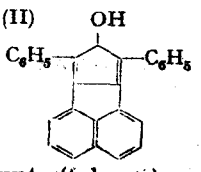


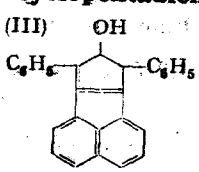
4.5-Diethylmalonyl-6.7.8.9-tetrahydroacenaphthene $C_{19}H_{22}O_2$, m. 88–89°. — **Fmn.** Similar to the foregoing compd. — **Rns.** Redn. → the corresp. **hydrocarbon** $C_{19}H_{26}$ [b. 190–5°/$_{16}$]. With fuming HNO_3 in a bomb at 140° → benzenepentacarboxylic acid and 2.2-diethylindan-1.3-dione-4.5.6-tricarboxylic acid (1920, 1921 Fleischer).

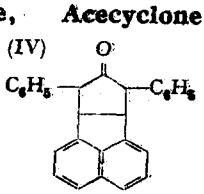
1910 Freund, Fleischer, *Ann.* 373 291.
1913 Freund, Fleischer, *Ann.* 399 182.
1914 Freund, Fleischer, *Ann.* 402 51.
1920 Fleischer, Siefert, *Ber.* 53 1255.
1921 Fleischer, Siefert, *Ann.* 422 272.

2.5 - Diphenyl - 3.4 - (1.8 - naphthylene) - cyclopentadienone, Acecyclone

(I) 

(II) 

(III) 

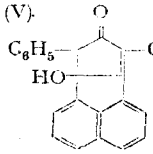
(IV) 

$C_{27}H_{16}O$, (I). Black cryst. (toluene), m. 289° in hot toluene violet, in H_2SO_4 red-violet and on long standing in H_2SO_4 brown. — **Fmn.** From acenaphthenequinone with dibenzyl ketone in boiling alc. KOH. — **Rns.** With Zn in acet. ac. → **2.5-diphenyl-3.4-(1.8-naphthylene)-cyclopentadienol** $C_{27}H_{18}O$, (II) [greenish needles, m. 182–3°, orange soln. in H_2SO_4] $\xrightarrow{\text{further redn.}}$ **2.5-diphenyl-3.4-(1.8-naphthylene)-Δ^3-cyclopentenol** $C_{27}H_{20}O$, (III) [greenish yellow needles, m. 229–30°, brown in contact with cold H_2SO_4, red-brown soln. on warming] $\xrightarrow{\text{boiling in acet.ac.}}$ **2.5-**

diphenyl-3.4-(1.8-naphthylene)-cyclopentanone $C_{27}H_{20}O$, (IV) [m. 229–30°, unchanged in cold H_2SO_4, yellow soln. on warming; *oxime* $C_{27}H_{21}ON$, m. 176–8°] (1935, 1938 Dilthey).

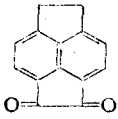
2.5-Diphenyl-4-hydroxy-3.4-(1.8-naphthylene)-Δ^2-cyclopentenone $C_{27}H_{18}O_2$, (V). Pale yellow cryst. (benzene), m. 230–1° (slow heating); deep red-violet soln. in H_2SO_4; pyr. soln. with Na methylate violet-blue. — **Fmn.** From acenaphthenequinone + dibenzyl ketone with cold alc. KOH (1935 Dilthey).

(V)



1935 Dilthey, ter Horst, Schommer, *J. pr. Ch.* [2] **143** 189.
1938 Dilthey, Henkels, Leonhard, *J. pr. Ch.* [2] **151** 97.

Pyracenehemiquinone, 5.6-Oxalylacenaphthene $C_{14}H_8O_2$. A yellow substance (m. 226°, in H_2SO_4 violet-red), which probably has this structure, is formed from acenaphthene and oxalyl bromide with $AlCl_3$ in CS_2.



1920 Fleischer, Wolff, *Ber.* **53** 925.

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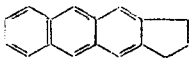
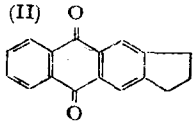
3. Tetracyclic Compounds with 1 Five- and 3 Six-Membered Rings

Naphtho-2′.3′:5.6-indan, 2.3-Cyclopentenoanthracene $C_{17}H_{14}$, (I). Leaflets (alc.), m. 242–3°; spar. sol. alc., ether, benz. — **Fmn.** From indan and phthalic anhydride with $AlCl_3$ in CS_2 → 5-o-carboxybenzoylindan, then with 15% oleum at 60–70° → 4.5- and 5.6-phthalylindan, the latter with Zn dust and 15% NH_3 → (I) (1920 v. Braun).

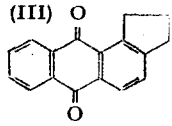
(I)



(II)



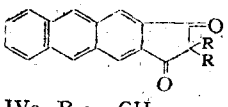
(III)



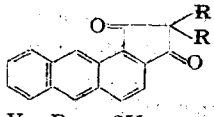
5.6-Phthalylindan, 2.3-Cyclopentenoanthraquinone $C_{17}H_{12}O_2$, (II). Needles (alc.), m. 180–1°. — **Fmn.** See above (1920 v. Braun).

4.5-Phthalylindan, 1.2-Cyclopentenoanthraquinone $C_{17}H_{12}O_2$, (III). Yellow, m. 108–110°. — **Fmn.** See above (1920 v. Braun).

2.3 (or 1.2)-Dimethylmalonylanthracene $C_{19}H_{14}O_2$, (IVa or Va). Brown-red plates or needles (alc.), m. 148.5–9.5°; eas. sol. hot benz., alc. and ether (red); H_2SO_4 red. — **Fmn.** From anthracene and dimethylmalonyl chloride with $AlCl_3$. — **Rns.** On boil. with KOH → isobutyrylanthracene-carboxylic acid (m. 203–5°). With CrO_3-acet. ac. → **dimethylmalonylanthraquinone** $C_{19}H_{12}O_4$, m. 231–2° (1913 Freund).



IVa, R = CH_3
IVb, R = C_2H_5



Va, R = CH_3
Vb, R = C_2H_5

2.3 (or 1.2)-Diethylmalonylanthracene $C_{21}H_{18}O_2$, (IVb or Vb). Yellow-red plates with MeOH and brown prisms with EtOH, m. 104–5° (solvent-free); in H_2SO_4 transient violet. — **Fmn.** As above with diethylmalonyl chloride. — **Rns.** On boil. with KOH → diethylacetyl-anthracenecarboxylic acid (m. 209–10°dec.). With CrO_3-acet. ac. → **diethylmalonylanthraquinone** $C_{21}H_{16}O_4$, m. 193–4° (1910, 1913 Freund).

1910 Freund, Fleischer, *Ann.* **373** 291. 1913 Freund, Fleischer, *Ann.* **399** 182.
1920 v. Braun, Kirschbaum, Schuhmann, *Ber.* **53** 1155.

1.2-Cyclopentenophenanthrene

HYDROCARBONS

1.2-Cyclopentenophenanthrene $C_{17}H_{14}$, needles (alc.), m. 135–136° (1933 Kon; 1934 b Cook), a 18.2, b 6.05, c 21.2 Å, β 119°; metastable: a 8.10, b 6.4, c 22.8 Å, β 90° (1935 Bernal). Absorpt. max. 217, 259, 280, 288, 301, 321, 336, 352 mμ (1935 Mayneord; 1933 Cook). — No oestrogenic activity (1934 a Cook). — **Synth.** From 1-(β-1-naphthylethyl)-cyclopentanol (1933 Cook), or ethyl 1-(β-1-naphthylethyl)-cyclopentan-2-one-1-carboxylate (1933 a Ruzicka) with H_2SO_4. From 2-(β-1-naphthylethyl)-cyclopentanol, 1-methyl-2-(β-1-naphthylethyl)- or 2-methyl-1-(β-1-naphthylethyl)-cyclopentanol by P_2O_5 (1933 Kon; 1934 Harper), or from 1-(β-1-naphthylethyl)-Δ^1-cyclopentene by $AlCl_3$ (1933 Cook) and Se dehydrogenation of the hydrocarbon mixt. — **Fmn.** By Se dehydrogenation of 3-hydroxy-1.2-cyclopentano-1.2.3.4.9.10.11.12-octahydrophenanthrene (1936 Hawthorne). By Clemmensen redn. of 3′-keto- or 5′-keto-1.2-cyclopentenophenanthrene (1935, 1937 Bachmann). — *Picrate* $C_{23}H_{17}O_7N_3$, m. 133–4° cor.; *compd. with sym. trinitrobenzene* $C_{23}H_{17}O_6N_3$, m. 165–6° cor.; *compd. with sym. trinitrotoluene* $C_{24}H_{19}O_6N_3$, m. 101–101.5° cor. (1933 a Ruzicka).

1.2-Cyclopenteno-9.10-dihydrophenanthrene $C_{17}H_{16}$, leaflets (MeOH), m. 65–9°. — **Fmn.** From 5′-keto-1.2-cyclopenteno-9.10-dihydrophenanthrene by Clemmensen redn. — **Rns.** Se dehydrogenation → the preceding hydrocarbon (1937 Burger).

1.2-Cyclopentano-1.2.3.9.10.11-hexahydrophenanthrene $C_{17}H_{20}$, b. 164–5°/3·. — **Fmn.** From the semicarbazone of 3-keto-1.2-cyclopentano-1.2.3.9.10.11-hexahydrophenanthrene with NaOEt in alc. (1936 Hawthorne).

1.2-Cyclopentano-1.2.3.4.9.10.11.12-octahydrophenanthrene $C_{17}H_{22}$, b. 201°/16·. — **Fmn.** By Clemmensen redn. of 3-keto-1.2-cyclopentano-1.2.3.4.9.10.11.12-octahydrophenanthrene. — **Rns.** Se dehydrogenation → 1.2-cyclopentenophenanthrene (1936 Hawthorne).

2-Methyl-1.2-cyclopentanoperhydrophenanthrene $C_{18}H_{30}$ is the parent hydrocarbon of the oestrogenic hormones and therefore the name **oestrane** is proposed by Adam, Danielli, Dodds, King, Marrian, Parkes, Rosenheim (1933 *Nature* 132 205). Oestrane derivatives are numbered according to the formula.

9-Methyl-1.2-cyclopentenophenanthrene $C_{18}H_{16}$, needles (MeOH), m. 109–10°. — **Fmn.** From β-(4-methyl-1-naphthyl)-ethyl-MgBr and 2-methyl-cyclopentanone, and then Se dehydrogenation. — *Picrate* $C_{24}H_{19}O_7N_3$, m. 153–54°; *compd. with sym. trinitrobenzene* $C_{24}H_{19}O_6N_3$, m. 170–71°; *styphnate* $C_{24}H_{19}O_8N_3$, m. 190–91°, dec. (1935 a Gamble).