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DIENE REACTIONS WITH DICYCLOHEXENYL

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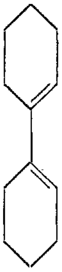
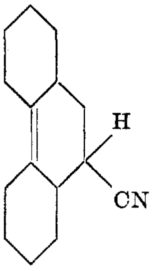
The reaction of dicyclohexenyl (I) with philodienic compounds constitutes a simple route to the phenanthrene series, but has been utilized mainly for the synthesis of polycyclic aromatic substances [maleic anhydride (1, 2, 3), benzoquinone (1, 3, 4, 7), α-naphthoquinones (1, 3), indones (3, 8), crotonic acid (5), cinnamic acid (3, 5, 6), benzylideneacetone (6), benzylideneacetophenone (6), *sym*-dibenzoylethylene (6), benzoylacrylic acid (6)]. The primary adducts of alicyclic character can also be considered as potential analogs of the morphine skeleton. A number of further diene reactions with (I) have, therefore, been studied, mainly with a view to preparing suitably substituted hydrogenated phenanthrenes.

Formula (II) of a 9-cyano-$\Delta^{4a,\,5a}$-dodecahydrophenanthrene for the nitrile obtained with acrylonitrile, was proven by dehydrogenation with selenium which gave 9-cyanophenanthrene in good yield. The hydrolysis of II presented unexpected difficulties; the amide was the main product even of prolonged treatment with alkali; only minor quantities of the acid were obtained in this way as well as by the interaction of the amide with nitrous acid. The amide could also not be converted into the corresponding amine by the Hofmann degradation.

Vinyl methyl ketone gave the well-crystallized ketone III, which could be converted into the corresponding hydrogenated 9-(α-hydroxyisopropyl)phenan-



I



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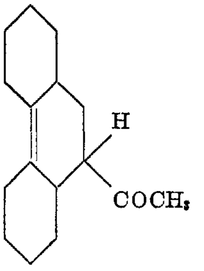

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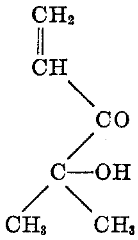
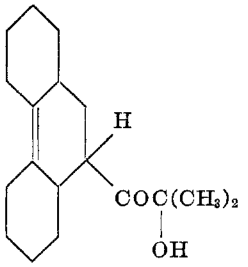
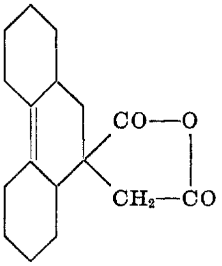


IV



V



VI

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threne by treatment with methylmagnesium iodide, and could also be characterized as the semicarbazone. The structure of III follows from the observation that the same compound is formed from II and methylmagnesium iodide. It is assumed also that in the following cases the Diels-Alder reaction takes the same course.

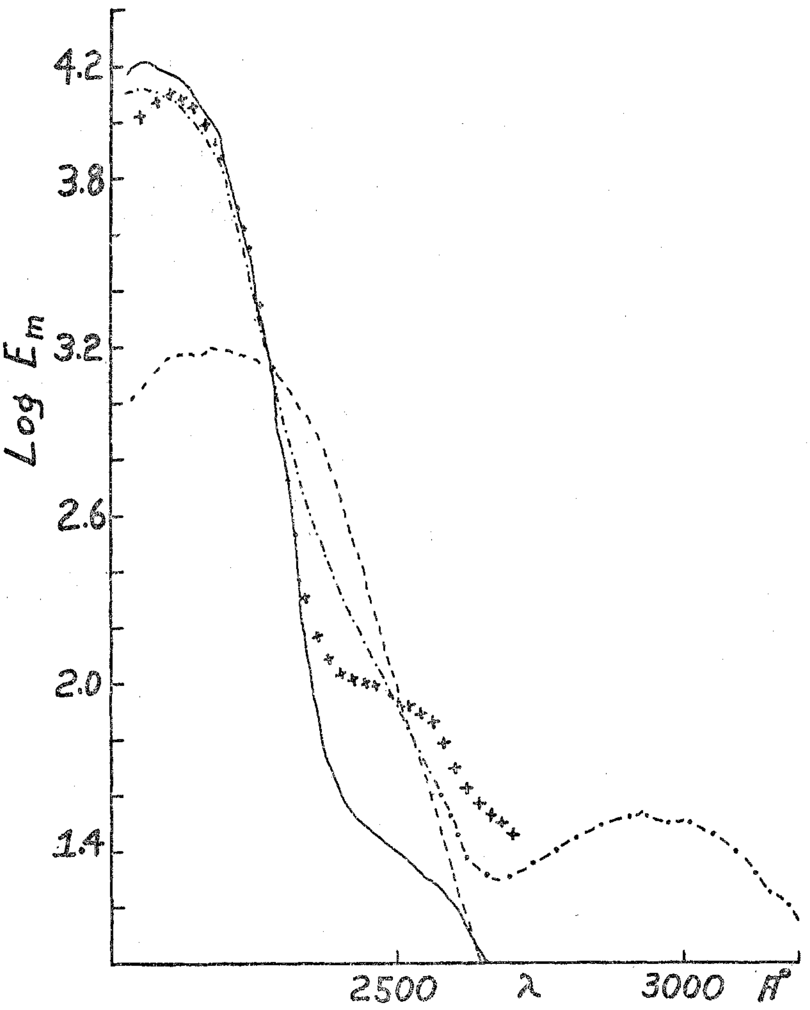


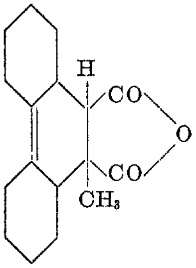
FIG. 1. ULTRAVIOLET ABSORPTION OF $\Delta^{4a, 5a}$-DODECAHYDROPHENANTHRENE-9-CARBOXYLIC ACID (++++) AND ITS AMIDE (II) (————), OF THE SEMICARBAZONE OF 9-ACETYL-$\Delta^{4a, 5a}$-DODECAHYDROPHENANTHRENE (III) (---), AND OF 9-(α-HYDROXYISOBUTYRYL)-$\Delta^{4a, 5a}$-DODECAHYDROPHENANTHRENE (V) (-•-•-•). Alcoholic solutions.

Vinyl α-hydroxyisopropyl ketone (IV) gave with dicyclohexenyl a crystalline ketone, assumed to be V which, like IV, failed to yield a semicarbazone.

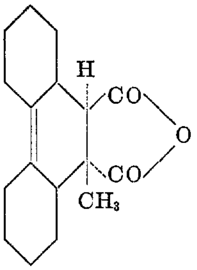
Infrared analysis,[2] however, revealed the presence of the carbonyl group (1698 cm^{-1}) and of the hydroxyl (3420 cm^{-1}), which appears modified by internal hydrogen bonding. The double bond did not show up appreciably in the spectrum; this is not unusual for tetrasubstituted ethylenes.

In none of the cases investigated was an attempt made to establish an exact proof for the *location of the double bond in the adducts*. Their ultraviolet absorption spectra showed that the double bond had not migrated into a position conjugated with the 9-substituent. The amide and the acid, corresponding to II, showed the following bands, respectively (in alcoholic solution): 2060 (log E_m 4.21) and 2460 Å (1.43); 2100 (4.09) and 2460 Å (1.99). The semicarbazone of III absorbed at 2180 Å (3.21), as expected for a saturated ketone (9, 10, 11). For V, the main band was found at 2066 Å (4.12) and a very weak second band at 2930 Å (1.54) (Fig. 1).[3]

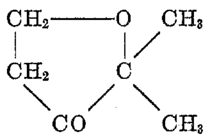
Finally, the interaction of I with itaconic acid was studied [for other diene reactions of itaconic acid, see (12, 13, 14)]. In boiling dioxane, an adduct was obtained which gave an anhydride for which formula VI is suggested. In order to prove that the diene reaction was not preceded by the isomerization to citraconic or mesaconic acid, I was also condensed with citraconic anhydride (probably to VII) and with mesaconic acid; the anhydride (probably VIII) of the latter adduct as well as VII were different from the anhydride (VI), obtained from itaconic acid.



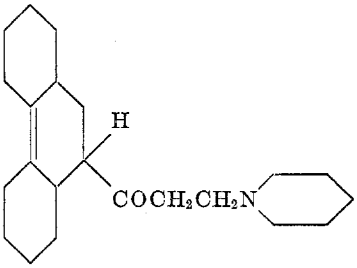
VII



VIII



IX



X

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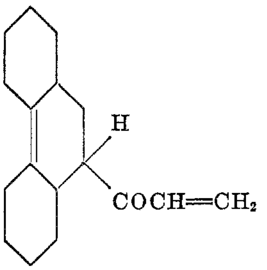
[2] The infrared analysis had been carried out by Dr. S. Pinchas, Optics Dept., Weizmann Institute of Science.

[3] We are indebted to Dr. Y. Hirshberg, Optics Dept., Weizmann Institute of Science, for the determination of these spectra.

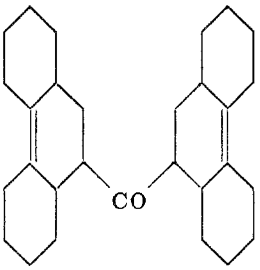
On the whole, these diene reactions proceeded homogeneously from the stereochemical point of view. Only in the case of V, were there definitely obtained (in a ratio of about 2:1) two isomeric products. It has not been decided whether they are stereoisomers or, what is more likely, substances differentiated by the location of the double bond (see ref. 6).

In addition to the two isomeric ketones, an isomer of IV was obtained in this reaction, which was characterized, in contradistinction to IV, by a semicarbazone. It is conceivable that IV isomerizes in some measure to 2,3-dimethyl-3-ketotetrahydrofuran (IX); a similar isomerization [of allyl α-hydroxyisopropyl ketone, to 2,2,5-trimethyl-3-ketotetrahydrofuran] has been observed by Nazarov and Torgov (15).

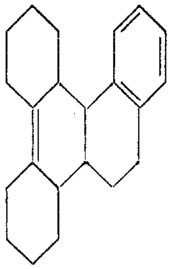
The ketone III underwent normally the Mannich reaction with formaldehyde and piperidine, when the reaction was carried out in isopropyl alcohol as solvent. Its reactivity was not sufficient to permit the desired condensation to proceed in *ethyl* alcohol; possibly the aldehyde is withdrawn under these conditions from the reaction mixture by acetal formation which is very much slower for secondary than primary alcohols (16, 16a). [The hydrochloride of the secondary base (buffered) acts as catalyst]. The aminoketone (X), which is characterized by its nitrate and salicylate, decomposes upon heating *in vacuo* to give a well crystallized product, very probably 9-acryloyl-$\Delta^{4a,5a}$-dodecahydrophenanthrene (XI); its α,β-unsaturated structure follows from its ability to react again with dicyclohexenyl, giving a product which analyzes for 9,9′-bis-($\Delta^{4a,5a}$-dodecahydrophenanthryl) ketone (XII).



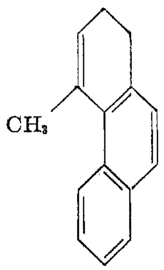
XI



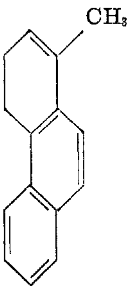
XII



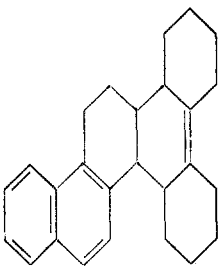
XIII



XIV



XV



XVI

In connection with these experiments, the possibilities of condensing I with a number of dienophilic aromatic hydrocarbons were studied. Diphenylacetylene (17), 9-cyanophenanthrene, and β-(9-phenanthryl)acrylic acid did not react even on prolonged heating at 280°. 1,2-Dihydronaphthalene, which is known to enter diene reactions with compounds of the tetraphenylcyclopentadienone type (18), reacted at 280° (not at 180°) to give in small yield a condensation product which analyzed correctly for the expected hydrogenated derivative (XIII)($C_{22}H_{28}$) of 1,2,3,4-dibenzphenanthrene. [For the synthesis of this system see (19, 20)]. Dehydrogenation of XIII with selenium proceeded only to the stage of a crystalline tetrahydro-1,2,3,4-dibenzphenanthrene. 4-Methyl-1,2-dihydrophenanthrene (XIV) and 1-methyl-3,4-dihydrophenanthrene (XV) even at 280° could not be induced to condense with dicyclohexenyl. But α-vinylnaphthalene (21–24) and dicyclohexenyl (I) at 250° gave a small yield of an oily adduct which should have formula XVI. This is a hydrogenated 1,2,3,4-dibenzochrysene, a ring system which appears to be unknown so far.

EXPERIMENTAL

9-Cyano-$\Delta^{4a,5a}$-dodecahydrophenanthrene. A mixture of 64 g. (0.4 mole) of dicyclohexenyl (I), 64 g. (1.2 moles) of acrylonitrile, and 1.2 g. of hydroquinone was refluxed (water-bath) for 18 hours. (In the absence of hydroquinone, a yellowish, resinous product is obtained.) After removal of the excess of acrylonitrile, the product was fractionated at 8 mm. After a small head fraction of dicyclohexenyl, a fraction boiling at 155–175° was obtained (40 g., 46%), about 50% of which crystallized when triturated with methanol at 0°. From methanol, this substance gave large colorless crystals of m.p. 84°. The oily part of the product could not be characterized, and its hydrolysis (*vide infra*) yielded the same amide as the crystalline product. It is possible that the oily product represents a second isomer (see text)· hydrolysis is then accompanied by inversion of the configuration.

Anal. Calc'd for $C_{15}H_{21}N$: C, 83.9; H, 9.9; N, 7.1.
Found: C, 83.7; H, 9.8; N, 6.7.

9-Cyanophenanthrene. The crystalline adduct (II) was heated with finely ground selenium at 350° for four hours. From methanol, the product separated in aggregates of fine needles, m.p. 108–111°. It did not depress the melting point of an authentic specimen of 9-cyanophenanthrene. Treatment of II with *bromine* in carbon tetrachloride solution led to copious evolution of hydrogen bromide, 9.5 atoms of bromine being consumed per molecule of II. The resinous reaction product, after removal of the solvent in *vacuo*, could be separated into two ill-defined, but crystalline substances, one, soluble in methanol, m.p. 80–100° (decomp.); the other, insoluble in methanol, but soluble in acetone, m.p. 170–180° (dec.).

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9-carboxylic acid and its amide. A mixture of 5 g. of II, 3 g. of sodium hydroxide, 3 cc. of water, and 25 cc. of *n*-butyl alcohol was refluxed for 9 hours. Upon cooling, the *amide* separated in fine needles, which were filtered, washed with butanol, and recrystallized from the same solvent. M.p. 250°.

Anal. Calc'd for $C_{15}H_{23}NO$: C, 77.2; H, 9.9; N, 6.0.
Found: C, 76.9; H, 10.4; N, 5.7.

By evaporation of the mother liquor from the recrystallization, a small second crop of material was obtained which melted at 267°, but on admixture of the main product at 255°. This may be an isomer of the above amide.

Anal. Calc'd for $C_{15}H_{23}NO$: C, 77.2; H, 9.9; N, 6.0.
Found: C, 77.0; H, 9.9; N, 5.8.

When acid was added to the alkaline original filtrate, a small quantity of the corresponding *acid* precipitated. After recrystallization from glacial acetic acid or benzene, it melted at 148–150°.

Anal. Calc'd for $C_{15}H_{22}O_2$: C, 77.2; H, 9.4.
Found: C, 77.7; H, 9.6.

Treatment of the amide with nitrous acid failed to yield the acid.

9-Acetyl-$\Delta^{4a,5a}$*-dodecahydrophenanthrene* (III). A mixture of 150 g. of I, 100 g. of the azeotrope (25) of methyl vinyl ketone, and 3 g. of hydroquinone was refluxed on the water-bath for 30 hours. The aqueous layer which separated was rejected and the product was fractionated at 4 mm. Between 100 and 150°, 48 g. of an oil distilled over, and a residue (171 g.) remained which crystallized upon cooling. The oil was fractionated again into a distillate of b.p. 70–130°/4 mm. (30 g.) and a crystallizing residue of 18 g. The solid product (189 g., 90%) was recrystallized twice from methanol and gave 143 g. of the pure ketone (III), m.p. 67–68°.

Anal. Calc'd for $C_{16}H_{24}O$: C, 82.5; H, 10.3.
Found: C, 82.3; H, 10.1.

The *semicarbazone*, from aqueous acetic acid, subsequently from butyl alcohol, formed small colorless prisms of m.p. 243° (dec.).

Anal. Calc'd for $C_{17}H_{27}N_3O$: C, 70.6; H, 9.3.
Found: C, 70.8; H, 9.4.

Slow concentration of the mother liquor of the ketone (III) gave a second crop, melting at 47–55°.

The *semicarbazone* prepared from this product had the same m.p. and gave the same analysis as that from the higher-melting product.

Anal. Calc'd for $C_{17}H_{27}N_3O$: C, 70.6; H, 9.3.
Found: C, 70.3; H, 9.6.

The same ketone (III) is obtained by reaction of II with methylmagnesium iodide: An ethereal solution of 2.2 g. of III was added to the Grignard solution, prepared from 0.75 g. of magnesium and 4.3 g. of methyl iodide. The mixture was refluxed for 2 hours, decomposed with ice-cold dilute sulfuric acid, and the ether residue heated on the steam-bath with a mixture of 5 cc. of acetone, 2 cc. of concentrated hydrochloric acid, and 5 cc. of water for 3 hours. Dilution with water and extraction with ether gave an oily product which was directly converted to the *semicarbazone*. After recrystallization from butyl alcohol, this melted at 243° (dec.) and gave no depression with the above-described product. Yield, 2 g. (70%).

Reaction with methylmagnesium iodide. The ketone (III) was added to a solution of methylmagnesium iodide (2 moles); when the lively reaction had subsided, the product was decomposed with ice and ammonium chloride and *9-(α-hydroxyisopropyl)-*$\Delta^{4a,5a}$*-dodecahydrophenanthrene* was isolated by distillation. It was a viscous oil of b.p. 161–163°/3 mm.

Anal. Calc'd for $C_{17}H_{28}O$: C, 82.3; H, 11.3.
Found: C, 82.0; H, 11.4.

(β-Piperidinoethyl) *(*$\Delta^{4a,5a}$*-dodecahydrophenanthryl-9) ketone hydrochloride* (X). Piperidine (15 g., 0.18 mole) was dissolved in 90 cc. of 2 *N* isopropylic hydrochloric acid, and paraformaldehyde (6 g.), III (20 g.; 0.09 mole), and 2-propanol (40 cc.) was added. The mixture was refluxed for 14 hours; after this time, addition of hot water to a small sample of the solution indicated that most of the ketone (III) had reacted. Upon cooling, the hydrochloride of X (14.5 g.) crystallized out; it was collected, washed with ether, and recrystallized from hot water or isopropyl alcohol (at 22°, 100 g. of isopropyl alcohol dissolves 20 g. of the aminoketone). It formed silky, glistening crystals, m.p. 188–189°.

Anal. Calc'd for $C_{22}H_{36}ClNO$: C, 72.2; H, 9.9.
Found: C, 72.0; H, 10.1.

The original mother liquor was evaporated *in vacuo* to dryness and the residue was freed from unchanged ketone (5 g.) by extraction with ether. The ether-insoluble part was treated with small quantities of water, which dissolves the excess piperidine hydrochloride, dried, and recrystallized from isopropyl alcohol and a little ether (which prevents crystallization of traces of the ketone III). Thus, a further 5 g. of the hydrochloride was secured. At 75% conversion, the yield was, therefore, 80%.

The *nitrate* of X, prepared from a hot aqueous solution of the hydrochloride and potassium nitrate, separates usually as an oil which crystallizes quickly. From water, small white crystals, m.p. 159° (dec.).

Anal. Calc'd for $C_{22}H_{36}N_2O_4$: C, 67.3; H, 9.2; N, 7.1.

Found: C, 67.1; H, 9.1; N, 7.0.

The *salicylate*, prepared analogously in alcoholic solution, formed pale yellow crystals which, after recrystallization from acetone, melted at 130–131°.

Anal. Calc'd for $C_{29}H_{41}NO_4$: C, 74.5; H, 8.8; N, 3.0.

Found: C, 74.2; H, 8.8; N, 3.2.

The condensation of III with paraformaldehyde and *diethylamine* hydrochloride in boiling isopropyl alcohol proceeded within 22 hours to the extent of 40% (recovery of 60% of unchanged ketone III); the aminoketone formed, could, however, not be isolated in a pure state. In boiling *ethyl* alcohol, practically all of the ketone remained unchanged within 22 hours. Also with piperidine hydrochloride in boiling ethyl alcohol, 75% of the ketone was recovered unchanged after 18 hours.

9-Acryloyl-$\Delta^{4a,5a}$-dodecahydrophenanthrene (XI). When the free aminoketone (obtained from its hydrochloride with ammonia) is heated *in vacuo*, piperidine is split off, and the unsaturated ketone (XI) distils over at 155°/4 mm., leaving a considerable (polymeric) residue. The ketone is a viscous, colorless oil.

Anal. Calc'd for $C_{17}H_{24}O$: C, 83.6; H, 9.9.

Found: C, 83.5; H, 10.0.

9,9′-Bis-($\Delta^{4a,5a}$-dodecahydrophenanthryl) ketone (XII) (?). A mixture of 8 g. of 9-acryloyldodecahydrophenanthrene, 9 g. of dicyclohexenyl, and 0.2 g. of hydroquinone was heated at 150–160° for seven hours and at 160–185° for a further six hours. The viscous reaction product was triturated twice with methanol, once with acetone, and eventually with ether; thus, a fine white crystalline powder was obtained (0.7 g.; 5%) which was recrystallized from benzene. Colorless crystals, m.p. 171–173°.

Anal. Calc'd for $C_{29}H_{42}O$: C, 85.7; H, 10.4.

Found: C, 86.0; H, 10.3.

9-(α-Hydroxyisobutyryl)-$\Delta^{4a,5a}$-dodecahydrophenanthrene (V) (?). A mixture of 50 g. of dicyclohexenyl (0.3 mole), 50 g. of α-hydroxyisopropyl vinyl ketone (IV) (26) (0.44 mole), and 2 g. of hydroquinone was heated at 100° for 21 hours. The product obtained was heated under 10 mm. pressure to a bath temperature of 173°. Thus, a *distillate* (32 g.) and a residue (A, 69 g.) was obtained.

The *distillate*, upon repeated redistillation, gave 8 g. of a fraction, boiling at 40–50°/10 mm.; 6 g. of an intermediate fraction, 50–105°/10 mm.; 9.5 g. of unchanged dicyclohexenyl; and 7.5 g. of residue B.

The first residue (A) was dissolved in 41 g. of hot ligroin (60–80°); upon cooling, 20 g. of V was obtained. The mother liquor was combined with residue (B) and fractionated again, giving 12 g. of a head fraction, mainly dicyclohexenyl, and 38 g. of a fraction of b.p. 160–185°/5 mm., from which, by dissolving in light petroleum ether and cooling a further 8 g. of ketone (V) was obtained. Colorless prisms, m.p. 92–93°; yield, 28 g. (34%).

Anal. Calc'd for $C_{18}H_{28}O_2$: C, 78.2; H, 10.1.

Found: C, 78.0; H, 10.0.

The *infrared spectum* of the product was measured in chloroform solution (0.105 g. and 1 cc. of solvent) in a cell of 0.1 mm. thickness.

The mother liquor of the second crop was distilled again and gave 22 g. of a viscous, colorless oil at 185°/4 mm., which gave the correct analysis for V.

Anal. Calc'd for $C_{18}H_{28}O_2$: C, 78.2; H, 10.1.

Found: C, 78.2; H, 10.0.

After prolonged standing at room temperature, crystallization set in; when the product was diluted with petroleum ether and kept at 0°, 14 g. (17%) of an *isomeric hydroxyketone* was secured, which crystallized from petroleum ether in large colorless crystals of m.p. 82–83°. Mixture m.p. with the ketone of m.p. 92–93°; 60–70°.

Anal. Calc'd for $C_{18}H_{28}O_2$: C, 78.2; H, 10.1.
Found: C, 78.2; H, 10.4.

The fraction of b.p. 40–50°/10 mm., which exhibited a pleasant smell (in contradistinction to the pungent odour of IV), gave a well-defined *semicarbazone* from a mixture of benzene and methanol as hexagonal prisms of m.p. 207°. The analysis pointed to an isomer of IV, possibly 2,2-dimethyl-3-ketotetrahydrofuran (IX).

Anal. Calc'd for $C_7H_{13}N_3O$: C, 49.1; H, 7.6; N, 24.6.
Found: C, 49.4; H, 7.7; N, 24.7.

Anhydride (VI) *of* $\Delta^{4a,5a}$*-dodecahydrophenanthrene-9-acetic-9-carboxylic acid* (?). A mixture of 6.5 g. (0.05 mole of itaconic acid, 8 g. (0.05 mole) of dicyclohexenyl, and 15 cc. of dioxane was refluxed for five hours. When the mass was poured out into boiling water, an oil separated, which crystallized spontaneously. The product was washed several times with warm water, dried, and triturated with petroleum ether; yield, 70%. The acid was dissolved in sodium bicarbonate solution which was then extracted with ether; finally, the acid was precipitated upon acidification of the extracted solution. When the resulting oil was extracted with petroleum ether and the filtered solution seeded, crystals of m.p. 199° (dec.) were obtained.

Anal. Calc'd for $C_{17}H_{24}O_4$: Neut. Equiv., 146. Found: Neut. equiv., 147.5.

The *anhydride*, which was prepared by heating at 200° or by refluxing with acetic anhydride, crystallized from methylcyclohexane and had m.p. 121.5°.

Anal. Calc'd for $C_{17}H_{22}O_3$: C, 74.5; H, 8.0.
Found: C, 74.7; H, 8.4.

cis-9-Methyl-$\Delta^{4a,5a}$*-dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride* (VII) (?). A mixture of 5.5 g. of citraconic anhydride and 8 g. of dicyclohexenyl was heated for 3 hours at 100°. From methylcyclohexane, the product crystallized; m.p. 112.5–113°. Yield, 12 g. (88.8%).

Anal. Calc'd for $C_{17}H_{22}O_3$: C, 74.5; H, 8.0.
Found: C, 74.8; H, 8.2.

trans-(VII) (?). A mixture of 10 g. of mesaconic acid, 12.5 g. of dicyclohexenyl, and 15 cc. of dioxane was refluxed for 5 hours; it was then poured into hot water. On standing in the cold, the *diacid* crystallized; m.p. 220–225° (dec.). Purification as described for the case of itaconic acid gave a product of sharp m.p. 225–226° (dec.).

Anal. Calc'd for $C_{17}H_{24}O_4$: Neut. equiv., 146. Found: Neut. equiv., 145.

The *anhydride*, prepared by refluxing with acetic anhydride, crystallized from petroleum ether and had m.p. 117–117.5°.

Anal. Calc'd for $C_{17}H_{22}O_3$: C, 74.5; H, 8.0.
Found: C, 73.9; H, 8.4.

All three compounds give melting point depressions with each other.

Adduct (XIII) (?). 1,2-Dihydronaphthalene was prepared (27) from the 1,4-isomer (28), b.p. 117°/49 mm., (22 cc.) by refluxing for 2 hours with 10% sodium ethoxide solution (100 cc.); b.p. 115°/51 mm.; yield, 17 g. A mixture of 8 g. of dicyclohexenyl and 6.5 g. of 1,2-dihydronaphthalene was heated at 280° for 24 hours (sealed tube) and subjected to distillation at 0.8 mm. At a bath temperature of 225–235°, a viscous oil was obtained in a yield of 4 g. (28%).

Anal. Calc'd for $C_{22}H_{28}$: C, 90.4; H, 9.6.
Found: C, 90.1; H, 9.9.

Tetrahydro-3,4,9,10-dibenzphenanthrene. After 4 g. of the adduct XIII had been heated with 5 g. of selenium at 320° for 20 hours, chloroform extracted small quantities of a hydrocarbon, which distilled under 0.1 mm. pressure at 205–215° (bath) and crystallized spontaneously. It was triturated with isopropyl alcohol, containing a little acetone, and recrystallized from the same solvent. Prisms, m.p. 147°.

Anal. Calc'd for $C_{22}H_{18}$: C, 93.6; H, 6.4.
Found: C, 93.4; H, 6.4.

Adduct (XVI) (?). Dicyclohexenyl (8.0 g.) and α-vinylnaphthalene (7.7 g., b.p. 120–125°/16 mm.) (29, 30) were heated at 250° for 24 hours. Distillation gave 2.5 g. (16%) of a viscous, yellow, green-fluorescent oil of b.p. 215°/0.3 mm.

Anal. Calc'd for $C_{24}H_{28}$: C, 91.1; H, 8.9.

Found: C, 90.8; H, 9.2.

Negative experiments. Dicyclohexenyl did not react with tolan (250°, 18 hours), nor did 9-cyanophenanthrene (31) (280°, 24 hours), β-(9-phenanthryl)acrylic acid [(32); crystallized from ethyl acetate, the acid forms prisms, m.p. 233°] (280°, 24 hours), 4-methyl-1,2-dihydrophenanthrene (XIV) (300°, 24 hours), or 1-methyl-3,4-dihydrophenanthrene (XV) (300°, 24 hours).

4-Methyl-1,2-dihydrophenanthrene (XIV). 4-Keto-1,2,3,4-tetrahydrophenanthrene (33) (6.4 g., b.p. 155–160°/0.8 mm.) was added to a Grignard solution, prepared from 0.8 g. of magnesium and 4.1 g. of methyl iodide. The crude carbinol was refluxed for two hours with 15 cc. of formic acid and gave the desired hydrocarbon as an oil, b.p. 135–140°/0.6 mm.

1-Methyl-3,4-dihydrophenanthrene (XV). 1-Keto-1,2,3,4-tetrahydrophenanthrene (33) (6.0 g., b.p. 155–160°/0.8 mm.) was treated as above. The solid crude product was refluxed with formic acid. The hydrocarbon, which distilled at 135–140°/0.6 mm., solidified immediately. M.p. 82° (33).

Anal. Calc'd for $C_{15}H_{14}$: C, 92.8; H, 7.2.

Found: C, 92.4; H, 7.0.

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