tion of desoxy compounds from primary hydroxyl groups.

The action of alkali on 1-tosyl-2,4-methylene-D,L-xylitol has resulted in the formation of a new 1,3-anhydro ring type among the sugar alcohol derivatives. The structure of the product as 1,3-anhydro-2,4-methylene-D,L-xylitol has been established conclusively.

A total of twenty-one new derivatives of 2,4-methylenexylitol and 2,4:3,5-dimethylene-D,L-xylitol have been described.

BETHESDA, MARYLAND RECEIVED OCTOBER 21, 1949

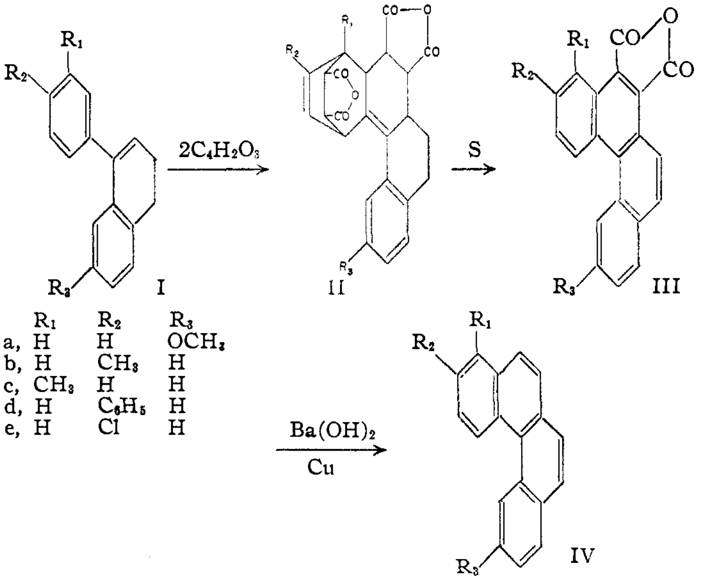
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Condensation of Phenylcycloalkenes with Maleic Anhydride. II. Synthesis of Substituted 3,4-Benzphenanthrenes[1]

BY JACOB SZMUSZKOVICZ[2] AND EDWARD J. MODEST[3]

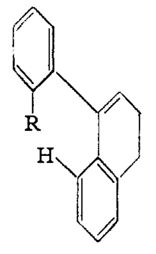
In continuation of our work on the reaction of phenylcycloalkenes with maleic anhydride,[4] we have successfully condensed various substituted dihydronaphthalenes with maleic anhydride and isolated the bis-adducts, which were dehydrogenated and then decarboxylated.

In case Ic the fact that the initial molecule of maleic anhydride adds to a position ortho rather than para to the methyl group was proved by decarboxylation of IIIc to the known 8-methyl-3,4-benzphenanthrene.[5]



	R_1	R_2	R_3
a,	H	H	OCH_3
b,	H	CH_3	H
c,	CH_3	H	H
d,	H	C_6H_5	H
e,	H	Cl	H

Maleic anhydride fails to add to 1-(*o*-tolyl)-3,4-dihydronaphthalene (Va) and to 1-(*o*-anisyl)-3,4-dihydronaphthalene (Vb), even under forcing conditions (220°).



V a, $R = CH_3$
b, $R = OCH_3$

A possible explanation for this lack of reactivity is that steric hindrance between the ortho substituent on the phenyl ring and the hydrogen atom at the peri position of the dihydronaphthalene ring forces the diene system out of coplanarity. Newman and Wheatley[6] have shown that optical activity of the 4,5-phenanthrene type is a result of a similar kind of steric interaction.

On decarboxylation of IIIa, IIId and IIIe, we obtained the new compounds 6-methoxy-, 7-phenyl- and 7-chloro-3,4-benzphenanthrene, respectively.

When there is a para methoxy substituent in the phenyl ring, the bis-adduct formed (VI) contains an enol–ether system which is easily ketonized by hot mineral acid.

A comparison of the properties of the two ketonized products reveals distinct dissimilarities. VIIb forms a semicarbazone but VIIa does not. Furthermore the ultraviolet absorption spectrum[7] of VIIb has maxima at 254 mμ (log *E* 4.04) and 293 mμ (log *E* 3.60), whereas that of VIIa exhibits only one maximum, at 253 mμ (log *E* 4.12). The maxima at 253 and 254 mμ are undoubtedly due to absorption of the styrene type.[8,9] The maximum at 293 mμ is due to keto-group absorption, the high value of the extinction coefficient arising from the superimposition effect.

---

[1] Presented before the Division of Organic Chemistry at the St. Louis meeting of the American Chemical Society, September 8 1948.

[2] Harvard University Postdoctoral Fellow 1947–1948; on leave of absence from the Weizmann Institute of Science, Rehovoth, Israel.

[3] Harvard University Ph.D. 1949; present address: Children's Medical Center, Boston, Mass.

[4] Szmuszkovicz and Modest, THIS JOURNAL, **70**, 2542 (1948).

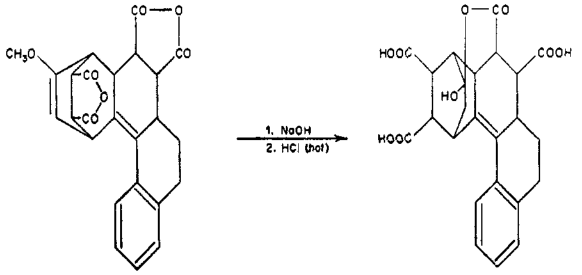
[5] Hewett, *J. Chem. Soc.*, 1286 (1938).

[6] Newman and Wheatley, THIS JOURNAL, **70**, 1913 (1948).

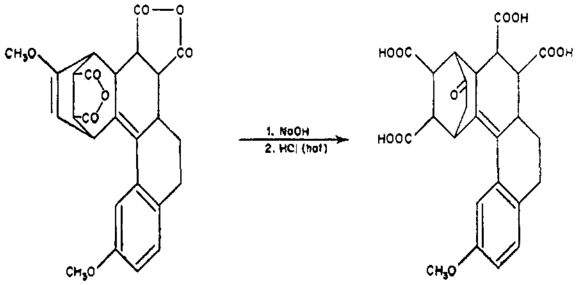
[7] The ultraviolet absorption spectra of aqueous solutions of VIIa and VIIb were measured with a Beckman model DU quartz spectrophotometer.

[8] Hillmer and Schorning, *Z. physik. Chem.*, **167A**, 407 (1933).

[9] Ramart-Lucas, *Bull. soc. chim.*, [5] **1**, 719 (1934).



VIa VIIa

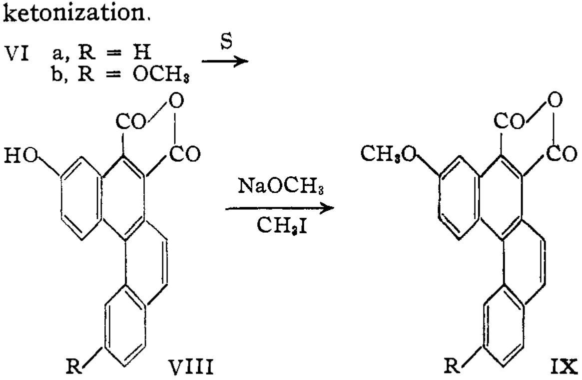


VIb VIIb

Other Diels–Alder adducts have been observed to undergo this type of transformation.[10,11] Bruckner and Kovács[11] have recently described the formation and ketonization of the bis-adduct of maleic anhydride and anethole. We propose structures for our ketonized products on the basis of our experimental observations together with those of Bruckner and Kovács. VIIa is most probably a hydroxylactone-tricarboxylic acid and VIIb a keto-tetracarboxylic acid.

The bis-adducts (VI) were aromatized to phenolic anhydrides (VIII). On treatment with sulfur both VIb and VIIb afford the same phenolic anhydride (VIIIb). Sulfur dehydrogenation of VIb to VIIIb probably proceeds through the keto-anhydride corresponding to VIIb, since the hydrogen sulfide evolved during the reaction may induce ketonization.

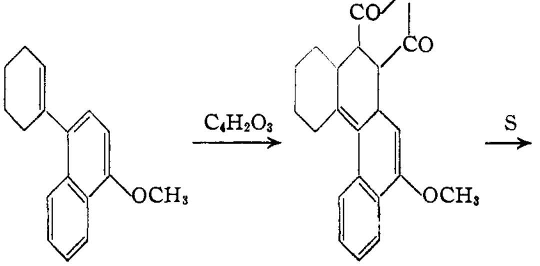
VI a, R = H $\xrightarrow{S}$
b, R = OCH_3



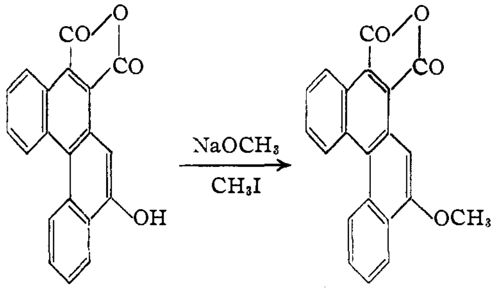
VIII IX

Zinc dust distillation of the barium salt of VIIIa produced 3,4-benzphenanthrene.

We obtained another phenolic anhydride (XII) from the reaction between 1-cyclohexenyl-4-methoxynaphthalene (X) and maleic anhydride according to the method of F. Bergmann and Szmuszkovicz.[12]



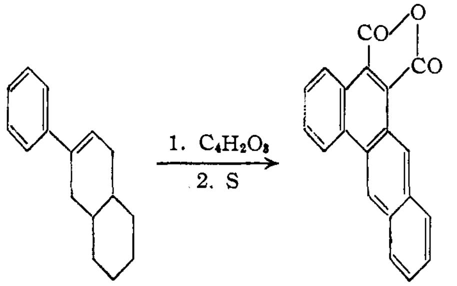
X XI



XII XIII

The three phenolic anhydrides (VIIIa, VIIIb, XII) are red to purple crystalline compounds, which cannot be crystallized from the usual solvents but are readily purified by sublimation. They are easily acetylated in refluxing acetic anhydride; the corresponding acetates have been prepared and characterized. Methylation of the phenolic anhydrides was accomplished with methyl iodide and sodium methoxide; IXa, IXb and XIII were formed.

The diene (XIV) was prepared from decalone-2 and phenylmagnesium bromide. We base our assumption of the location of the alicyclic double bond in XIV on the fact that decarboxylation of XV leads to 1,2-benzanthracene, not chrysene.



XIV XV

Decarboxylation of IXa and IXb afforded 7-methoxy-3,4-benzphenanthrene[4] and 2′,6-dimethoxy-3,4-benzphenanthrene. Thus our application of the Diels–Alder reaction with phenyldihydronaphthalenes, in addition to providing an efficient synthesis of the parent hydrocarbon, leads to a variety of substituted 3,4-benzphenanthrenes.

---

(10) Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **11**, 661 (1941) [*C. A.*, **36**, 1593 (1942)].

(11) Bruckner and Kovács, *Nature*, **161**, 651 (1948); *J. Org. Chem.*, **13**, 641 (1948).

(12) F. Bergmann and Szmuszkovicz, THIS JOURNAL, **69**, 1367 (1947).

Acknowledgment.—The authors wish to express their appreciation to Professor Louis F. Fieser for his kind interest and support during this investigation and to Mrs. Mary Fieser for her advice and assistance in preparing the manuscript. The microanalyses were performed by Mrs. Shirley R. Golden.

Experimental[13]

Preparation of Starting Materials.—The phenylcycloalkenes were prepared by the Grignard reaction. The reagent was made from 0.1 mole of the appropriate halide and 2.5 g. of magnesium in ether. After a benzene solution of the ketone had been added, the reaction mixture was refluxed for five hours and let stand overnight. It was decomposed with saturated ammonium chloride solution and washed as usual, and the solvent was evaporated. Dehydration of the crude carbinol residue was accomplished with 20 g. of potassium bisulfate for one hour at 160°. An ether solution of the dehydrated product was washed with water, dilute alkali, water and saturated sodium chloride solution, and dried; the diene was obtained by distillation *in vacuo*.

1-Phenyl-7-methoxy-3,4-dihydronaphthalene,[14] 1-(*p*-anisyl)-3,4-dihydronaphthalene,[14] 1-(*p*-tolyl)-3,4-dihydronaphthalene[15] and 1-(*o*-anisyl)-3,4-dihydronaphthalene[16] were all prepared according to literature. 1-(*o*-Tolyl)-3,4-dihydronaphthalene was synthesized by the method of Friedel, Orchin and Reggel[17]; we also failed to obtain a good analytical sample. We prepared 1-(*p*-xenyl)-3,4-dihydronaphthalene according to F. Bergmann, Szmuszkovicz and Fawaz,[18] except that we used *p*-iododiphenyl instead of *p*-bromodiphenyl. 1-(*p*-Chlorophenyl)-3,4-dihydronaphthalene was prepared by the directions of F. Bergmann and Szmuszkovicz.[19] We succeeded in isolating it in crystalline form; prismatic columns from methanol, m. p. 94.4–94.7°.

Anal. Calcd. for $C_{16}H_{13}Cl$: C, 79.83; H, 5.44. Found: C, 79.69; H, 5.48.

1-(*m*-Tolyl)-3,4-dihydronaphthalene.—This compound was synthesized from 15.5 g. of *m*-bromotoluene, 2.26 g. of magnesium and 12 g. of tetralone-1. The mixture was refluxed for three hours, left overnight, and decomposed with 10% sulfuric acid. Distillation yielded 10.9 g. (60.5%) of yellow oil, b. p. 140–148° (0.02 mm.). A sample was redistilled for analysis, b. p. 146° (0.02 mm.).

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.49; H, 7.27.

1-(*p*-Anisyl)-7-methoxy-3,4-dihydronaphthalene.—A Grignard reaction was carried out with 18.7 g. of *p*-bromoanisole, 2.5 g. of magnesium, and 14 g. of 7-methoxytetralone-1 in ether–benzene solution. After the addition of the ketone, ether was evaporated and the benzene solution was refluxed for sixteen hours. The Grignard complex was decomposed in the usual manner. Dehydration was conducted for one hour in refluxing 88% formic acid. Distillation afforded 11 g. (52.4%) of yellow oil, b. p. 178–180° (0.001 mm.).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.18; H, 6.81. Found: C, 81.60; H, 6.34.

1-Cyclohexenyl-4-methoxynaphthalene.—1-Methoxynaphthalene (79 g.) in 350 cc. of chloroform was treated for one hour with a solution of 80 g. of bromine in 70 cc. of chloroform in the presence of 68 g. of sodium acetate. Occasional cooling was necessary. The mixture was then stirred for one hour at room temperature and washed with water, dilute alkali and water. 1-Methoxy-4-bromonaphthalene boiled at 140–150° (0.1 mm.), mostly at 148–150° (0.1 mm.); 101 g. (84.9%).

The Grignard reagent was prepared from 35.6 g. of 1-methoxy-4-bromonaphthalene, 7.4 g. of magnesium and 21.3 g. of methyl iodide as entrainer. Cyclohexanone (30 g.) was added in the cold and the mixture was refluxed for three hours. After evaporation of the solvent, heating on the steam-bath was continued for three hours. The solution was decomposed with saturated ammonium chloride and dehydrated with sodium bisulfate at 160° for an hour. The desired material distilled at 165–175° (0.6 mm.), (20 g., 57%). The picrate was formed in ethanol and crystallized as red needles, m. p. 150–151°.

Anal. Calcd. for $C_{23}H_{21}O_8N_3$: C, 59.1; H, 4.5. Found: C, 59.4; H, 4.6.

The picrate was decomposed and distillation afforded a white oil, which crystallized from dilute ethanol in the form of elongated rods melting at 44–45°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.4; H, 7.9.

2-Phenyl-1,4,5,6,7,8,9,10-octahydronaphthalene.—Prepared from 17.3 g. of bromobenzene, 2.75 g. of magnesium, and 15.22 g. of *trans*-decalone-2, this phenylcycloalkene boiled at 133–140° (0.1 mm.), mostly at 135° (0.1 mm.), a colorless oil (14.8 g., 69.7%) which solidified immediately. Crystallized from methanol it formed colorless prisms melting at 57–59°.

Anal. Calcd. for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.64; H, 9.69.

Condensation with Maleic Anhydride (Table I).—In the condensations the ratio of phenylcycloalkene to maleic anhydride was 1:2.5 by weight. The temperature of the reaction varied from 125 to 160° and the time from sixteen to twenty-four hours. The brown, oily product was dissolved in the minimum quantity of acetic acid and left to crystallize for two days. All the crystalline addition products isolated proved to be bis-adducts, with the exception of the adduct of 1-cyclohexenyl-4-methoxynaphthalene. In every case the filtrate obtained after separation of the crystalline material was treated with water, and the gummy precipitate which formed turned solid after it had been cooled and scratched. This solid, which contains some copolymeric material, could be dehydrogenated according to the directions in Table II for the crystalline adduct. The corresponding aromatic anhydride was produced in 30–40% yield.

1-Cyclohexenyl-4-methoxynaphthalene Adduct (XI).—A mixture of 10 g. of 1-cyclohexenyl-4-methoxynaphthalene and 20 g. of maleic anhydride was heated for five hours at 160°. After the addition of 10 cc. of acetic acid it was allowed to stand for twenty-four hours. The few crystals that deposited were filtered and found to be fumaric acid (m. p. 285°). The addition of a little water to the filtrate caused the precipitation of a white substance which was washed well with water, m. p. 220° (3.5 g., 25%). Crystallization from acetic acid yielded small plates melting at 222–223°. The analysis indicates that it is the free acid.

Anal. Calcd. for $C_{21}H_{22}O_5$: C, 71.2; H, 6.3. Found: C, 71.0; H, 6.2.

Ketonization of VIa.—Two hundred milligrams of VIa was dissolved in a solution of 0.5 g. of sodium hydroxide in 2 cc. of water by heating on the steam-bath for a short time. Upon the addition of 7 cc. of concentrated hydrochloric acid, an oily material appeared together with some sodium chloride. Water (5 cc.) was added and heating continued for one-half hour. Crystallization of the product (VIIa) occurred during this period of heating; white crystals, m. p. 256–257°. Hygroscopic plates melting at 257–258° were obtained by crystallization from water.

Anal. Calcd. for $C_{24}H_{22}O_9$: C, 63.32; H, 5.10. Found: C, 63.43; H, 4.88.

All attempts to form the semicarbazone of this compound failed.

Ketonization of VIb.—The reaction was carried out as in the preceding case. After the acidified solution had been

---

[13] All melting points are corrected.

[14] Howell and Robertson, *J. Chem. Soc.*, **587** (1936).

[15] Braun and Anton, *Ber.*, **67**, 1051 (1934).

[16] Orchin, THIS JOURNAL, **70**, 495 (1948).

[17] Friedel, Orchin and Reggel, *ibid.*, **70**, 199 (1948).

[18] F. Bergmann, Szmuszkovicz and Fawaz, *ibid.*, **69**, 1773 (1947).

[19] F. Bergmann and Szmuszkovicz, *ibid.*, **70**, 2748 (1948).

TABLE I

PHENYLCYCLOALKENE BIS-ADDUCTS

Adduct	Reaction temp., °C.	Reaction time, hr.	Yield cryst. material, %	M. p., °C.	Crystal form	Solvent for cryst.	Formula	Analyses, % Calcd. C	H	Found C	H
IIa	125	36	37.6	243.8–244.8	Plates[a]	HOAc	$C_{25}H_{20}O_7$	69.44	4.66	69.60	4.22
IIb	150–160	16	40.8[b]	332–333	Prisms[c]	Ac_2O	$C_{26}H_{20}O_6$	72.10	4.85	71.87	4.86
IIc	150–160	17	35.0[b]	343–344	Prisms[c]	Ac_2O	$C_{25}H_{20}O_6$	72.10	4.85	71.70	4.86
IId	150	24	59.2	325–326	Prisms	[d]	$C_{30}H_{22}O_6$	75.30	4.64	75.37	4.69
IIe	150	24	44.0	346–347	Prisms	[d]	$C_{24}H_{17}O_6Cl$	65.83	4.14	66.08	3.79
VIa	150–160	20	20.5	325	Plates	HOAc	$C_{25}H_{20}O_7$	69.44	4.66	69.39	4.74
VIb	150–160	16	46.0	280–281	Prisms	Ac_2O	$C_{26}H_{22}O_8$	67.53	4.80	67.66	4.72

[a] Analytical sample dried for twenty-four hours at 150°. [b] Additional material was obtained by extraction of the aqueous acetic acid filtrate with ether. [c] Must be thoroughly dried before analysis. [d] Submitted for analysis directly from the reaction mixture after trituration with boiling acetic anhydride, acetic acid and cold methanol.

TABLE II

AROMATIC ANHYDRIDES

Aromatic anhydride	React. temp., °C.	React. time, min.	Sublim. temp., °C. at 0.001 mm.	% Yield of crude material	M. p., °C. Crude	Pure	Crystal form	Solvent for cryst.	Formula	Analyses, % Calcd. C	H	Found C	H
IIIa	235–290	16	240–280	80	200–205[a]	226–227	Clust. of vermilion ndls.	Ac_2O	$C_{21}H_{12}O_4$	76.82	3.69	76.64	3.55
IIIb	255–280	10	270–285	89	265–267	291–292	Yell. ndls.	Ac_2O	$C_{21}H_{12}O_3$	80.76	3.86	80.68	3.94
IIIc	260–265	10	220–280	87	205–210	236–237	Yell. ndls.	HOAc	$C_{21}H_{12}O_3$	80.76	3.86	80.75	3.91
IIId	250–290	35	250–300	90	245–255[b]	272–273	Yell. ndls.	Ac_2O	$C_{26}H_{14}O_3$	83.41	3.78	83.40	3.83
IIIe	255–270	30	240–250	77	268–270	274–275	Elongated orange rods	Ac_2O	$C_{20}H_9O_3Cl$	72.19	2.73	72.29	2.83
VIIIa	250–260	35	270–300	60	310–315	342–343	Brick-red prisms	[c]	$C_{20}H_{10}O_4$	76.43	3.21	76.58	3.36
VIIIb	250–260	35	250–300	70	285–290	296–297	Violet prisms	[d]	$C_{21}H_{12}O_5$	73.25	3.21	73.16	3.36

[a] By fractional crystallization from acetic acid a small amount of yellow crystals, insufficient for analysis, could be isolated: yellow needles from acetic acid, melting at 289–290°. [b] A small amount of yellow substance, insufficient for analysis, was isolated by crystallization from acetic acid: yellow needles, m. p. 249–251°. [c] The phenolic anhydride was purified by sublimation only. [d] This compound could not be crystallized from a solvent; for purification it was dissolved in hot dioxane, precipitated with water and resublimed.

heated for thirty minutes, a clear solution resulted which deposited crystals overnight, m. p. 290–292°. Crystallization from water afforded hygroscopic needles (VIIb), which swelled at 220°, resolidified, and melted at 297–298° (dec.).

Anal. Calcd. for $C_{25}H_{24}O_{10}\cdot H_2O$: C, 59.63; H, 5.22. Found: C, 59.47; H, 5.41.

A solution of VIIb (100 mg.), semicarbazide hydrochloride (200 mg.), and sodium acetate (300 mg.) in 4 cc. of water was heated for fifteen minutes on the steam-bath. Overnight microcrystals of the semicarbazone separated m. p. above 350°.

Anal. Calcd. for $C_{26}H_{27}O_{10}N_3$: C, 57.67; H, 5.03. Found: C, 57.29; H, 5.42.

Dehydrogenation (Table II).—The hydroaromatic adducts were aromatized with sulfur. We employed in most instances 50% excess sulfur, which caused the reaction temperature to be lowered and which could be easily separated from the product during subsequent sublimation. The yields for dehydrogenation given in Table II refer to those cases in which crystalline bis-adduct was used as starting material.

9-Hydroxy-3,4-benzphenanthrene-1,2-dicarboxylic Acid Anhydride (XII).—One gram of XI was heated with 360 mg. of sulfur at 220–290° for one-half hour. Sublimation at 230–300° (0.1 mm.) afforded a crystalline red material melting at 332–334°. When it was dissolved in boiling dioxane and water was added to the point of cloudiness, a microcrystalline red substance was obtained. After resublimation at 295° (0.005 mm.), it melted at 338–339°, with considerable shrinking above 320°.

Anal. Calcd. for $C_{20}H_{10}O_4$: C, 76.43; H, 3.21. Found: C, 76.30; H, 3.22.

2′-Hydroxy-6-methoxy-3,4-benzphenanthrene-1,2-dicarboxylic Acid Anhydride (VIIIb) from VIIb.—VIIb was dehydrogenated with sulfur. The reaction started at 275° and was conducted up to 300° for sixteen minutes. Sublimation at 295–310° (0.005 mm.) yielded purple-red crystals, which were purified by dissolution in dioxane, precipitation with water, and sublimation, m. p. 296°; mixed m. p. with VIIIb (Table II) showed no depression.

1,2-Benzanthracene-3,4-dicarboxylic Acid Anhydride (XV).—One gram of XIV was heated with 2.5 g. of maleic anhydride for twenty-four hours at 150–160°. The viscous brown mass was dissolved in acetic acid and precipitated with water. The off-white precipitate, m. p. 80–100°, was mixed with 1.36 g. of sulfur and heated for thirty-eight minutes at 225–285°. Sublimation at 260–330° (0.01 mm.) yielded 430 mg. of a dark brown substance, m. p. 180–200°. For purification this crude material was extracted twice with small portions of boiling benzene and then crystallized from acetic acid; dark orange rods, m. p. 248–250°. This compound could also be crystallized from dioxane.

Anal. Calcd. for $C_{20}H_{10}O_3$: C, 80.53; H, 3.38. Found: C, 80.38; H, 3.49.

Acetylation of VIIIa.—Acetylation of 200 mg. of VIIIa was carried out in 10 cc. of refluxing acetic anhydride for four hours. A brown precipitate, m. p. 250–255°, resulted when the acetic anhydride solution was cooled. Two crystallizations from acetic anhydride afforded elongated golden rods, m. p. 258–259.5° (started subliming at 250°).

TABLE III

METHYLATED PRODUCTS

Compd.	M. p., °C.	Crystal form	Cryst. solvent	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
IXa	214.5–215.5	Orange-red need.[a]	HOAc	$C_{21}H_{12}O_4$	76.82	3.69	77.08	3.98
IXb[b] A	211.5–214.5	Orange hex. plates	Ac_2O	$C_{22}H_{14}O_5$	73.74	3.94	73.86	3.92
IXb B	209.5–212	Orange rods[c]	Ac_2O	$C_{22}H_{14}O_5$	73.74	3.94	73.69	4.01
XIII	272–274.3	Orange-red rods	Ac_2O	$C_{21}H_{12}O_4$	76.82	3.69	76.75	3.63

[a] Purified first by sublimation at 220–250° (0.001 mm.), then by crystallization. [b] Initial purification by sublimation at 230–300° (0.05 mm.). Dimorphic crystalline modifications, A and B, separated by fractional crystallization from acetic anhydride. [c] The orange rods slowly change into hexagonal plates, if left in contact with the mother liquor, and must be filtered very quickly in order that a pure product may be obtained.

TABLE IV

SUBSTITUTED 3,4-BENZPHENANTHRENES

3,4-Benzphenanthrene	Yield,[a] %	M. p., °C.	Crystal form	Cryst. solvent	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
6-Methoxy	76	78–79	Leaflets	CH_3OH	$C_{19}H_{14}O$	88.34	5.46	88.29	5.74
picrate		119–120	Orange ndls.	CH_3OH	$C_{25}H_{17}O_8N_3$	61.60	3.52	61.67	3.21
2′,6-Dimethoxy	32[b]	107.5–107.8	Prismatic rods	CH_3OH	$C_{20}H_{16}O_2$	83.31	5.59	83.18	5.65
picrate		155–156	Crimson rods	C_2H_5OH	$C_{26}H_{19}O_9N_3$	60.35	3.70	60.56	3.36
7-Phenyl	90	138–139	Plates	HOAc	$C_{24}H_{16}$	94.70	5.30	94.80	5.35
picrate		122–123	Red prisms	HOAc[c]	$C_{36}H_{22}O_{14}N_6$	56.70	2.91	56.37	3.23
7-Chloro	25[d]	103–104	Plates	C_2H_5OH	$C_{18}H_{11}Cl$	82.28	4.22	82.02	4.23
picrate		113–114	Orange blocks	C_2H_5OH	$C_{24}H_{14}O_7N_3Cl$	58.61	2.87	58.97	2.44

[a] Yields are based on crude decarboxylated products. [b] Purification effected by adsorption on alumina. The analytical sample was obtained after elution with 30–60° petroleum ether and crystallization from methanol. [c] This picrate, which contains two molecules of picric acid to one of the hydrocarbon, is easily decomposed if washed with polar solvents. [d] In this case incomplete decarboxylation results unless application of water-pump suction is delayed until 340°. The crude yellow oil obtained was dissolved in ligroin and adsorbed on a column of 80-mesh alumina. Elution with ligroin, followed by three crystallizations of the colorless substance resulting, provided a pure sample.

Anal. Calcd. for $C_{22}H_{12}O_5$: C, 74.15; H, 3.40. Found: C, 74.10; H, 3.38.

Acetylation of VIIIb.—The phenolic anhydride (VIIIb) was acetylated by the method described above. On evaporation of the solution to dryness an orange material was obtained, m. p. 185–188°. It was purified by sublimation at 230–250° (0.001 mm.); m. p. 189–190°.

Anal. Calcd. for $C_{23}H_{14}O_6$: C, 71.51; H, 3.66. Found: C, 71.75; H, 3.90.

Acetylation of XII.—The acetate of XII was crystallized twice from acetic anhydride, brown rods melting at 256–258°. It was sublimed for analysis at 250° (0.001 mm.), m. p. unchanged.

Anal. Calcd. for $C_{22}H_{12}O_5$: C, 74.15; H, 3.40. Found: C, 74.07; H, 3.59.

Methylation (Table III).—The phenolic anhydrides were methylated by the following general procedure, which is based upon numerous trial runs. Methylation was first attempted with dimethyl sulfate but that reagent proved unsatisfactory.

To a solution of 50 mg. of sodium in 5 cc. of methanol were added 100 mg. of the phenolic anhydride and 2 cc. of methyl iodide. The clear, blood-red solution was refluxed for fifteen hours, during which period the color changed to light orange. The solution was evaporated almost to dryness in a current of air and the residue was dissolved by reflux for thirty minutes in a solution of 2 g. of sodium hydroxide in 8 cc. of water and 10 cc. of methanol. Methanol was removed by evaporation in a current of air and the aqueous solution was refluxed for one hour in an oil-bath, water being added, if necessary, to keep the sodium salt in solution. After acidification of the solution with concentrated hydrochloric acid and digestion for five minutes on the steam-bath, the crude methylated product was obtained in quantitative yield.

Decarboxylation (Table IV).—Decarboxylation was conducted with a mixture of aromatic anhydride (0.5 g.), crystalline barium hydroxide (2.5 g.), and copper–bronze (0.7 g.) in a tube at 320–360° for thirty minutes. Water-pump suction was applied just as soon as the reaction started.

8-Methyl-3,4-benzphenanthrene (IVc).—Decarboxylation of IIIc afforded a yellow oil (25% yield), which was converted into the picrate in ethanol. After two crystallizations from that solvent, red needles were obtained, m. p. 110–111°. Hewett[5] has reported m. p. 107–108° for the picrate of 8-methyl-3,4-benzphenanthrene.

7-Methoxy-3,4-benzphenanthrene.—A sample of 2′-methoxy-3,4-benzphenanthrene-1,2-dicarboxylic acid anhydride (IXa) was decarboxylated by the usual procedure. The picrate of the decarboxylated material was formed in ethanol, m. p. 119–120°. Crystallization from ethanol containing picric acid afforded crimson needles, m. p. 120.5–121.5°. Mixed m. p. with the picrate of 7-methoxy-3,4-benzphenanthrene, obtained by decarboxylation of 7-methoxy-3,4-benzphenanthrene-1,2-dicarboxylic acid anhydride,[4] showed no depression.

Zinc Dust Distillation of VIIIa.—The barium salt of the phenolic anhydride VIIIa was formed by addition of a hot dioxane solution of the compound to 5 cc. of water containing 1 g. of crystalline barium hydroxide. The precipitate was dried at 200°, mixed with 7 g. of zinc dust, and distilled at 400° through a layer of zinc dust in a slow stream of nitrogen. A colorless oil resulted, which formed a picrate in ethanol, m. p. 125–126°, identical with that of 3,4-benzphenanthrene (mixed m. p. determination).

Summary

1. The Diels–Alder condensation with maleic anhydride has been achieved with a series of substituted phenylcycloalkenes.
2. 6-Methoxy-, 2′,6-dimethoxy-, 7-phenyl- and 7-chloro-3,4-benzphenanthrene have been prepared.
3. An interesting enol-ether type cleavage has been observed.

CAMBRIDGE 38, MASSACHUSETTS RECEIVED JULY 29, 1949