tor and yellow amorphous material precipitated which was filtered and recrystallized from acetic acid to give anthraquinone VII (0.065 g., 85%) m.p. 347–350°, identical in all respects to that prepared in *A* above.

3-Nitronaphtho[*b*]*cyclobutene* (XI). Naphtho[*b*]cyclobutene (1.54 g.) was added slowly with stirring to 70% nitric acid (1.53 g.) cooled by an ice bath to 0°. The reaction mixture became dark and viscous, but became lighter as the yellow crystalline nitro derivative appeared. After 1 hr., the ice bath was removed and the reaction allowed to run its course at room temperature for an additional 3 hr. As the reaction progressed, stirring became very difficult and more nitric acid (*ca.* 2 ml.) was added. The mixture was nearly a solid mass at the end of the reaction. Water was added and the crystalline material filtered, washed with 5% aqueous sodium bicarbonate, then water, and dried. Three crystallizations from ethanol gave yellow-orange needles (0.80 g., 40%), m.p. 129.0–130.5°. A fourth recrystallization gave the analytical sample, m.p. 131.0–131.5° (corr.).

Anal. Calcd. for $C_{12}H_9O_2N$: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.24; H, 4.71; N, 6.94.

Ultraviolet spectrum (ethanol): λ_{max} 244 (log ϵ 3.85) 342 (3.77).

3-Aminonaphtho[*b*]*cyclobutene* (XII). A mixture of 3-nitronaphtho[b]cyclobutene (0.20 g.), 10%, palladium on carbon (0.01 g.), excess hydrazine hydrate[5] (0.5 ml.), and 95% ethanol (20 ml.) was refluxed for 1 hr. and filtered hot. Water (*ca.* 20 ml.) was added to the filtrate until it became cloudy, and the mixture cooled in the refrigerator. The small white needles (0.12 g.) m.p. 91.0–91.5°, were filtered and dried. Concentration of the filtrate yielded an additional 0.02 g. of amine XII (total yield: 82%), which was recrystallized from petroleum ether (b.p. 30–60°).

Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.32; H, 6.68; N, 8.30.

Ultraviolet spectrum (ethanol): λ_{max} 241 (log ϵ 4.42) 311 (3.66).

Permanganate oxidation of 3-aminonaphtho[*b*] *cyclobutene.* Two per cent aqueous potassium permanganate solution was added drop by drop to a suspension of amine XIII (32 mg.) in water (5 ml.) until the reaction solution remained pink. The excess permanganate was decomposed by formaldehyde and the manganese dioxide removed by filtration. The slightly yellow solution was passed through a column of hydrochloric acid–washed Amberlite IR 120 (washed with distilled water until chloride ion test was negative). The acid fraction (eluate was tested with Alkacid paper) was collected and the water evaporated *in vacuo* to give a light brown paste which was sublimed at atmospheric pressure to give white needles (10 mg.), identified as phthalic anhydride by infrared analysis. The infrared spectrum showed no trace of pyromellitic or succinic anhydrides.

2,3-Dimethyl-1-nitronaphthalene was prepared by the procedure of Willstaedt.[8] After several crystallizations from ethanol it melted at 111° (reported[8] m.p. 111°).

Ultraviolet spectrum (ethanol): λ_{max} 269 (log ϵ 358), 307 (3.02), 321 (3.02).

2,3-Dimethyl-1-aminonaphthalene. To a solution of 2,3-dimethyl-1-nitronaphthalene (2.0 g.) in 95% ethanol (35 ml.) was added hydrazine hydrate (8 ml.) and 10% palladium on carbon (0.15 g.). The mixture was refluxed for 2 hr., filtered, and diluted with water until cloudy. Slow evaporation of the alcohol at room temperature resulted in the precipitation of pink leaflets (1.62 g., 95%), m.p. 48–50° (reported,[8] m.p. 42°). Neither sublimation, distillation (177° at 14 min.) nor crystallization from petroleum ether changed the melting point. Because of the discrepancy with the reported melting point, elemental analyses were carried out.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.33; H, 7.80; N, 8.38.

Ultraviolet spectrum (ethanol): λ_{max} 244 (log ϵ 4.47) 320 (3.63), shoulder at 328 mμ.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation and by a Fellowship from the Nitrogen Division, Allied Chemical Corp. This aid is gratefully acknowledged.

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[8] H. Willstaedt, *Svensk. Kem. Tid.*, **54**, 223 (1942).

[CONTRIBUTION FROM THE CHEMISCHES INSTITUT]

Synthesis of Some Methyl-Substituted Anthracenes

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Received October 17, 1960

A new route to the synthesis of a variety of methyl-substituted anthracenes is described. *o*-Dibromobenzene, or its homolog, is metallated with butyllithium to give benzyne, or its homolog, which is treated with furan or methyl-substituted furans to give 1,4-epoxy-1,4-dihydronaphthalenes. The latter, as dienophiles, are condensed with methyl-substituted butadienes, and the products dehydrated, and then dehydrogenated to produce the methylated anthracenes. These products have been used to study the bathochromic effect of the methyl group on the ultraviolet spectrum maxima of anthracene.

When fluorobenzene is treated with phenyllithium the fluorine atom becomes unusually active and is easily replaced by a phenyl group to give, after hydrolysis, biphenyl. Wittig[3] first suggested that this reaction probably proceeds *via* the intermediate, benzyne, or dehydrobenzene. Since that time many other reactions involving metallation of halogenated benzenes have been explained in terms of such an intermediate.[4–6]

One of the best indications that benzyne is actually formed, though short-lived, is the fact, discovered by Wittig,[7] that the product is a dieno-

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[1] Present address: Calvin College, Grand Rapids, Mich.

[2] This work was done at the University of Heidelberg under a National Science Foundation Faculty Fellowship, 1959–60.

[3] G. Wittig, *Naturwissenschaften*, **30**, 696 (1942).

[4] G. Wittig, *Angew. Chem.*, **69**, 245 (1957).

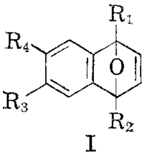
[5] R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

[6] J. D. Roberts, *Chem. Soc. Symposia*, Bristol, 1958, Special Publication No. 12, p. 115.

[7] G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

TABLE I

METHYL-SUBSTITUTED 1,4-EPOXY-1,4-DIHYDRONAPHTHALENES



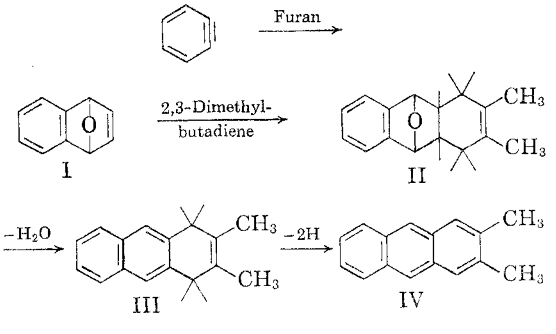
I

No.	R_1	R_2	R_3	R_4	Yield, %	M.P.[a]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	H	H	H	H	70	56[b]	$C_{10}H_8O$				
2[c]	CH_3	H	H	H	56	Liq.[d]	$C_{11}H_{10}O$	83.51	83.55	6.37	6.18
3[e]	CH_3	CH_3	H	H	45	35–35.5	$C_{12}H_{12}O$[f]	83.68	83.75	7.02	6.82
4[g]	H	H	CH_3	H	54	Liq.[h]	$C_{11}H_{10}O$	83.51	83.09	6.37	6.63
5[i]	H	H	CH_3	CH_3	55	72.5–73	$C_{12}H_{12}O$	83.68	83.93	7.02	6.89
6	CH_3	CH_3	CH_3	CH_3	25	52–52.5	$C_{14}H_{16}O$	83.96	84.01	8.05	8.31

[a] All melting points in this paper are corrected. [b] Ref. (7). [c] The 2-methylfuran used was distilled over sodium, b.p. 64°/750 mm., n_D^{20} 1.4322. [d] B.p. 57–59°/0.2 mm., n_D^{20} 1.5510. [e] The 2,5-dimethylfuran, ref. (9), was distilled over sodium, b.p. 92–93°/750 mm., n_D^{20} 1.4413. [f] This compound was isomerized with boiling methanolic hydrochloric acid to give 80% 4-methyl-1-naphthol, m.p. 82–83°. [g] The 3,4-dibromotoluene was prepared from *p*-toluidine by bromination followed by the Sandmeyer reaction giving b.p. 58–60°/0.4 mm., n_D^{20} 1.5970. Dauben and Tilles[10] report n_D^{30} 1.5822. [h] B.p. 57–59°/0.2 mm., n_D^{20} 1.5510. [i] The 4,5-dibromo-1,2-dimethylbenzene was prepared by the method of Mills and Nixon,[11] m.p. 88°.

phile and reacts as such with furan and other dienes. Such reactions have interesting applications for they make possible the synthesis of a variety of fused ring systems. Furthermore, the product of the reaction with furan, 1,4-epoxy-1,4-dihydronaphthalene, is also a dienophile and reacts in turn with other dienes to extend the polycyclic system.

The present investigation was concerned with the synthesis of methyl-substituted anthracenes. Benzyne was condensed with furan or methyl-substituted furans to give methyl-substituted 1,4-epoxy-1,4-dihydronaphthalenes, of type I. The latter were then treated with methyl-substituted butadienes and the products, like II, successively dehydrated to III and dehydrogenated to give the desired methyl-substituted anthracenes, IV. A typical series of reactions is as follows:



The preparation of benzyne and its reaction with furans was carried out essentially as described previously,[8] except that *o*-dibromobenzene was added to the butyllithium-furan mixture. The furans used were: furan, 2-methylfuran, 2,5-dimethylfuran. The following *o*-dibromobenzenes were used: *o*-dibromobenzene, 3,4-dibromotoluene, and 4,5-dibromo-1,2-dimethylbenzene. The products, type I are listed in Table I, all of which are new except compound 1.[7]

Compounds of type I were condensed with methyl-substituted butadienes in two different ways. At first the reaction was accomplished without a solvent and under pressure at 150°, since the preliminary trials in xylene as solvent were not successful. Later, however, the reaction was found to proceed equally well in a very small amount of xylene at reflux temperature. In either case a small amount of hydroquinone was usually added to minimize polymerization of the diene. The butadienes used were: isoprene, 1,3-dimethylbutadiene, and 2,3-dimethylbutadiene. The products of this reaction, type II, are listed in Table II. None of these compounds has been reported previously.

Dehydration of the type II compounds was accomplished most efficiently by adding a little concentrated hydrochloric acid to the boiling methanolic solution of the compound. The reaction is an exothermic one, decidedly so in those instances where the epoxy compound contains methyl substituents in the 9 and/or 10 positions. It is likely that the initial step in this reaction is the protonation of the epoxy oxygen atom, which is facilitated by the increased electron charge on this atom contributed by the methyl groups on the adjacent carbon atoms. The products, type III, are listed

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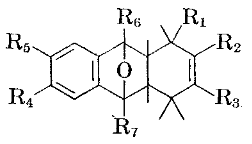
(8) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **79**, 2625 (1957).

(9) E. Campaigne and W. Foye, *J. Org. Chem.*, **17**, 1405 (1952).

(10) W. Dauben and H. Tilles, *J. Am. Chem. Soc.*, **72**, 3185 (1950).

(11) W. Mills and I. Nixon, *J. Chem. Soc.*, 2510 (1930).

TABLE II. METHYL-SUBSTITUTED 9,10-EPOXY-1,4,4a,9,9a,10-HEXAHYDROANTHRACENES

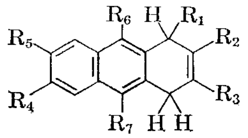


II

No.	Method	R_1	R_2	R_3	R_4	R_5	R_6	R_7	Yield, %	Solvent of Crystn.	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1[a]	A	H	CH_3	H	H	H	H	H	30	Pet. ether	58–58.5	$C_{15}H_{16}O$	84.87	84.97	7.60	7.48
2[b]	A	H	CH_3	CH_3	H	H	H	H	86	Methanol	108.8–109	$C_{16}H_{18}O$	84.91	85.11	8.02	8.21
3[c]	A	CH_3	H	CH_3	H	H	H	H	92[d]		Liq.[d]	$C_{16}H_{18}O$				
4	B	H	CH_3	CH_3	H	H	CH_3	H	82	Methanol	96.5–97	$C_{17}H_{20}O$	84.96	84.83	8.39	8.23
5	B	H	CH_3	CH_3	H	H	CH_3	CH_3	80	Methanol	100–100.5	$C_{18}H_{22}O$	84.99	84.92	8.72	8.90
6	A	H	CH_3	CH_3	CH_3	H	H	H	77	Pet. ether	107–107.5	$C_{17}H_{20}O$	84.96	84.99	8.39	8.23
7	B	H	CH_3	CH_3	CH_3	CH_3	H	H	85	Pet. ether	155.2–155.4	$C_{18}H_{22}O$	84.99	85.31	8.72	8.83
8	B	H	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	77	Pet. ether	141.5–142	$C_{20}H_{26}O$	85.05	85.08	9.28	9.36

[a] The isoprene used was freshly distilled, b.p. 34°/745 mm., n_D^{20} 1.4216. [b] The 2,3-dimethylbutadiene was freshly distilled, b.p. 69–70°/750 mm., n_D^{20} 1.4370. [c] The 1,3-dimethylbutadiene was freshly distilled, b.p. 75–76°/750 mm. [d] Yield is that of the crude oil. It decomposed on attempted distillation, and was used in the next step without purification.

TABLE III. METHYL-SUBSTITUTED 1,4-DIHYDROANTHRACENES



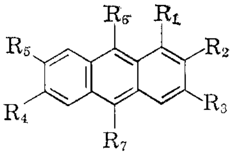
III

No.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	Solvent of Crystn.	Yield, %	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	H	CH_3	H	H	H	H	H	Methanol	73	98.5–99	$C_{15}H_{14}$	92.74	92.63	7.26	7.23
2	H	CH_3	CH_3	H	H	H	H	Ethanol	63	189–190[a]					
3	CH_3	H	CH_3	H	H	H	H	Pet. ether	49[b]	54–54.5	$C_{16}H_{16}$	92.21	92.16	7.74	7.55
4	H	CH_3	CH_3	H	H	CH_3	H	Ethanol	90	112–112.5	$C_{17}H_{18}$	91.84	91.80	8.16	8.17
5	H	CH_3	CH_3	H	H	CH_3	CH_3	Ethanol-benzene, 3:1	94.5	178.5–179[c]	$C_{18}H_{20}$				
6	H	CH_3	CH_3	CH_3	H	H	H	Methanol	48.5	195–196 d.[d]	$C_{17}H_{18}$	91.84	91.91	8.16	8.14
7	H	CH_3	CH_3	CH_3	CH_3	H	H	Ligroin	47	250.5–251 d.[e]	$C_{18}H_{20}$	91.47	91.64	8.53	8.48
8	H	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	Ligroin	96.5	211–212	$C_{20}H_{24}$	90.85	91.03	9.15	8.97

[a] Jadot and Roussel[12] report m.p. 185°. [b] Yield based on unpurified II. [c] Jadot and Roussel[12] report m.p. 177.5°; Fieser and Webber[13] report m.p. 175.3–176.3°. [d] Immersed in melting point bath at 190°. [e] Immersed at 240°.

TABLE IV

METHYL-SUBSTITUTED ANTHRACENES



IV

No.	Method	R_1	R_2	R_3	R_4	R_5	R_6	R_7	Solvent of Crystn.	Yield	M.P.	Formula
1	A	H	CH_3	H	H	H	H	H	Pet. ether	35	206-206.5[a]	$C_{15}H_{12}$
2	A	H	CH_3	CH_3	H	H	H	H	Pet. ether	51	250.5-251[b,c]	$C_{16}H_{14}$
3	A	CH_3	H	CH_3	H	H	H	H	Methanol	68	79-79.5[d,e]	$C_{16}H_{14}$
4	B	H	CH_3	CH_3	H	H	CH_3	H	Ethyl acetate	99	124-124.5[f]	$C_{17}H_{16}$
5	B	H	CH_3	CH_3	H	H	CH_3	CH_3	Pet. ether	97	138.3-138.8[g]	$C_{18}H_{18}$
6	A	H	CH_3	CH_3	CH_3	H	H	H	Pet. ether	30	249-249.5[h,i]	$C_{17}H_{16}$
7	B	H	CH_3	CH_3	CH_3	CH_3	H	H	Ethyl acetate	97	299-300[j]	$C_{18}H_{18}$
8	B	H	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	Ethyl acetate	98	223-224[k]	

[a] Melting points reported generally vary from 200 to 209°. [b] Fairbourne[16] reports m.p. 246°. [c] Barnett and Marrison[17] report m.p. 252°. [d] Fieser and Heymann[18] report m.p. 78.2-79.6°. [e] Clemo and Ghatge[19] report m.p. 78°. [f] Barnett and Marrison[17] report m.p. 125°. [g] Fieser and Webber[13] report m.p. 139.4-140.2°. [h] Morgan and Coulson[20] report m.p. 255°. [i] Carruthers[21] reports m.p. 244-245°. [j] Carruthers[21] reports m.p. 292-293°. [k] *Anal.* Calcd.: C, 91.55; H, 8.45. Found: C, 91.26; H, 8.65.

in Table III. Two of these compounds, numbers 2[12] and 5,[13] have been reported previously.

Dehydrogenation of the 1,4-dihydroanthracenes, III, was done in some cases with selenium but the yields were generally low. Nearly quantitative yields were easily obtained by using chloranil as oxidizing agent in xylene as solvent at reflux temperature. In order to avoid difficulties in removing excess chloranil from the product, care should be taken to use no more than the theoretical amount of this reagent. Table IV lists the methyl-substituted anthracenes, IV, one of which is new, namely, 2,3,6,7,9,10-hexamethylanthracene.

One interesting fact deserves mention. As a rule the melting points of the compounds in the foregoing synthesis increase with each step. However, there is one exception to this rule, namely, the change from 2,3,9,10-tetramethyl-1,4-dihydroanthracene to 2,3,9,10-tetramethylanthracene, in which case the melting point drops about 40°. These data confirm those published for these two compounds.[13]

Effect of methyl substitution on the ultraviolet spectrum of anthracene. One of the objectives of this study was to obtain a variety of substituted anthracenes in order to examine the effect of methyl-substitution on the positions of the ultraviolet spectrum maxima.

The ultraviolet absorption spectrum of anthracene has two rather distinct parts, one with maxima in the 240-260 mμ range (41,670 cm.$^{-1}$ to 38,460 cm.$^{-1}$), the other between 290 and 380 mμ (34,480 and 26,310 cm.$^{-1}$). It has been suggested[14,15] that these parts are related to different types of electronic excitations. On this theory the 240-260 mμ maxima are associated primarily with electronic shifts, and therefore polarization, along the horizontal axis, while the 290-380 mμ maxima are related to polarization along the vertical axis of the anthracene molecule. The spectra of anthracenes containing unsaturated, or conjugatable, substituents strongly suggests the plausibility of this theory. But even methyl groups, though they have a smaller effect, also are reported to show the same trend. Jones[14,15] has examined the bathochromic shifts due to methyl and other substituents in various positions using the data available for four such compounds. We have now obtained the spectra of the compounds prepared in this study, and present herewith additional data on the bathochromic effect of methyl substituents in anthracene.

Table V presents the spectral data for the compounds synthesized by the method outlined in

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(12) J. Jadot and J. Roussel, *Bull. soc. roy. sci. Liège*, **23**, 69 (1954).

(13) L. Fieser and T. Webber, *J. Am. Chem. Soc.*, **62**, 1360 (1940).

(14) R. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

(15) R. Jones, *Chem. Revs.*, **41**, 353 (1947).

(16) A. Fairbourne, *J. Chem. Soc.*, 1573 (1921).

(17) E. Barnett and F. Marrison, *Ber.*, **64**, 535 (1931).

(18) L. Fieser and H. Heymann, *J. Am. Chem. Soc.*, **64**, 376 (1942).

(19) G. Clemo and N. Ghatge, *J. Chem. Soc.*, 1068 1(956).

(20) G. Morgan and E. Coulson, *J. Chem. Soc.*, 2551 (1929).

(21) W Carruthers, *J. Chem. Soc.*, 603 (1956).

TABLE V

ABSORPTION SPECTRA DATA ON METHYL-SUBSTITUTED ANTHRACENE[a]

Compound	Principal Maxima									
	mμ	log ε	mμ	log ε	mμ	log ε	mμ	log ε	mμ	log ε
Anthracene (A)	253	5.48	324	3.54	339	3.83	356	4.02	375	4.01
2-Methyl A	255	5.48	[b]		340	3.65	358	3.80	377	3.75
2,3-Dimethyl A	257	5.60	326	3.57	341	3.83	358	3.97	378	3.91
2,3,6-Trimethyl A	259	5.50	[b]		342	3.70	360	3.82	379	3.72
2,3,6,7-Tetramethyl A	261	5.64	328	3.53	343	3.73	359	3.85	379	3.73
2,3,9-Trimethyl A	261	5.57	333	3.59	350	3.87	368	4.04	388	3.99
2,3,9,10-Tetramethyl A	265	5.34	342	3.40	359	3.71	379	3.90	400	3.81
2,3,6,7,9,10-Hexamethyl A	269	5.16	343	3.11	360	3.38	380	3.54	402	3.45
1,3-Dimethyl A	257	5.38	[b]		344	3.72	360	3.87	381	3.83

[a] Solvent: cyclohexane. [b] These maxima were not distinct enough to permit accurate measurement.

TABLE VI

BATHOCHROMIC SHIFTS IN THE ANTHRACENE SPECTRUM DUE TO METHYL SUBSTITUTION

	Anthracene Spectrum Maxima				
	257 mμ 39,520 cm.$^{-1}$	324 30,910	339 29,500	356 28,090	375 26,670
Position of Methyl Groups	Bathochromic Shift in cm.$^{-1}$				
2	300		90	160	140
2,3	600	230	180	160	230
2,3,6	910		260	310	280
2,3,6,7	1200	420	350	230	280
2,3,9	1200	880	930	910	890
2,3,9,10	1780	1670	1640	1700	1670
2,3,6,7,9,10	2350	1760	1720	1780	1790
1,3	610		430	310	420

this paper. Only the principal maxima are given for comparison with each other. Of the compounds listed, only the spectra of 1,3-di-[18] and 2,3,9,10-tetramethylanthracene[13] have been reported.

Table VI shows the bathochromic shifts of the principal maxima. The values for the shifts are given in wave numbers to facilitate comparison with other literature data on such shifts. Examination of these data reveals a number of interesting facts which we now discuss briefly.

Methyl substitution has the largest bathochromic effect on the shortest intense maximum, 39,520 cm.$^{-1}$ The shift per methyl group is very nearly 300 cm.$^{-1}$ (2 mμ) and is additive to a remarkable degree. On the other hand, a *beta* methyl group has a smaller effect upon the other maxima of longer wave length, and, except for the 29,500 cm.$^{-1}$ band, there is no semblance of additivity in the shifts. Our data on 2-methylanthracene confirm the prediction of Peters[22] that a *beta*-methyl group should cause a bathochromic shift of 2 mμ in the p-band (26,670 cm.$^{-1}$) of anthracene. His calculations are based upon the assumption that the shift is due to conjugation of the methyl group with the parent hydrocarbon resulting in a perturbation of the molecular orbitals of anthracene.

Methyl substitution in the *meso* position has a very pronounced effect on all the spectral maxima of anthracene. In the case of the shortest wave-length band (39,520 cm.$^{-1}$) the frequency shift per methyl group is about 600 cm.$^{-1}$, a value twice as great as that due to a *beta*-methyl substituent. These results agree fairly well with those reported for 9-methyl- and 9,10-dimethylanthracene.[23] It should also be noted that, as in the case of *beta* substitution, *meso* substitution also causes a shift of the shortest wave-length maximum which is additive.

With respect to the effect of *meso*-methyl substitution on the longer wave-length maxima, it is clear that the bathochromic shifts are much larger

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(22) D. Peters, *J. Chem. Soc.*, 646 (1957).

(23) L. Fieser and J. Hartwell, *J. Am. Chem. Soc.*, 60, 2555 (1938).

and are more consistently so than those caused by *beta*-substitution, and are fairly additive. The shift per methyl group of the 375 $\mathrm{m}\mu$ band (*p*-band) agrees well with the theoretical prediction of Peters,[22] and the uniformly large effect of *meso*-methyl substitution confirms the observations on the spectra of 9-methyl- and 9,10-dimethylanthracene.[15]

An adequate theoretical explanation of the observed shifts is not readily at hand. Most theoretical treatments of the bathochromic effect of alkyl substituents assume the conjugative effect to predominate, the methyl group being regarded as a modified vinyl group. On this assumption the effect of conjugation would be to reduce the energy of the excited state, the degree of such reduction varying with the number and positions of the methyl substituents, and the effect upon the different spectral maxima depending upon the positions of the substituents, that is, upon the direction of polarization.

There is no doubt a qualitative correspondence between the bathochromic shifts due to methyl and clearly conjugatable substituents which points to such conjugation and polarization along mutually perpendicular axes of the molecule. However, as Jones[15] has observed, alkyl groups in the 9 and/or 10 positions have a uniformly large effect upon *all* the spectral maxima while unsaturated groups in these positions have a far more selective effect. Our data on the *beta*-substituted anthracenes also show that, although there is a selective bathochromic effect favoring the shortest wave-length maximum, the effect upon the longer wavelength maxima cannot be ignored.

In summary, then, our additional data confirm the theory that the conjugative effect of methyl groups is important, and that, therefore, the positions of these groups account for their selective bathochromic effects upon the various spectral maxima of anthracene. However, there must be other factors also affecting these shifts. The theory of Jones[15] that the ground state energy is also modified by alkyl substituents seems to provide at least a qualitative explanation for the general bathochromic shifts of all the maxima of the anthracene spectrum.

EXPERIMENTAL

General method for making methyl-substituted 1,4-epoxy-1,4-dihydronaphthalenes. n-Butyllithium in ether, 50 ml. of 1.10*N* solution (0.055 mole) was added to a flask previously evacuated and then filled with pure nitrogen, and cooled to −70°. Furan, or a methyl-substituted furan, 30 ml., freshly distilled, was added below 55° during about 15 min., after which there was added, during 30 min. at −70° to −55°, a solution of 11.8 g. (0.050 mole) *o*-dibromobenzene, or an equivalent amount of its homolog, distilled over phosphorus pentoxide, in 20 ml. of dry ether. During this addition, and for 40 min. more at −70° to −55°, the mixture was stirred vigorously. After allowing it to warm to 0°, 100 ml. of water was added, the layers separated, the aqueous layer washed twice with ether, the washings added to the ether layer and washed with water to remove any alkali. After drying over potassium carbonate, most of the ether and unused furan were recovered by fractionation. The residue was either fractionated further, in case the product was a liquid, or crystallized from petroleum ether (b.p. 60–80°) in those cases where the product was a solid.

Condensation of 1,4-epoxy-1,4-dihydronaphthalenes with dienes. Method A. The epoxy compound, 0.02 mole, the diene, 0.022 mole, and a few small crystals of hydroquinone were sealed in a pressure tube (15-ml. cap.) after flushing out the air with dry nitrogen. It was heated over night at 140–150°, cooled, and the volatile materials removed *in vacuo.* The crude product was boiled with methanol, and the polymerized diene removed by filtration. The product was recovered from the filtrate by crystallization, or by distillation in case it was a liquid.

Method B. The epoxy compound, 0.02 mole, the diene, 0.022 mole, and a few small crystals of hydroquinone were dissolved in 4 ml. of xylene and heated at reflux temperature over night. The volatile materials were removed *in vacuo* and the crude product was extracted with methanol and worked up as in method *A*.

Dehydration of epoxy compounds to form methyl-substituted 1,4-dihydroanthracenes. Methyl-substituted 9,10-epoxy-1,4,4a,9,9a,10-hexahydroanthracene, 0.01 mole, was dissolved in 60 ml. of methanol. At reflux temperature 6 ml. of concd. hydrochloric acid was carefully added through the condenser. The mixture was refluxed overnight in most cases, although 2 hr. were found to be enough for the 9- and/or 10-methyl-substituted compounds. In all cases the crystalline product precipitated soon after the acid addition. After cooling several hours in the refrigerator the product was filtered, washed with cold methanol, and dried *in vacuo* at room temperature. In some cases it was pure without further crystallization.

Dehydrogenation of methyl-substituted 1,4-dihydroanthracenes. Method A. Methyl-substituted 1,4-dihydroanthracene, 0.01 mole, was mixed with 0.01 mole of selenium powder and heated in an oil bath for 4 to 8 hr. at 270–300°, or until no more hydrogen selenide was evolved. After cooling, the product was extracted with petroleum ether or benzene, clarified with carbon, evaporated to dryness and recrystallized.

Method B. Methyl-substituted 1,4-dihydroanthracene, 0.01 mole and 0.01 mole of chloranil were dissolved in 40 ml. of dry xylene and heated at reflux temperature for 1 hr. After cooling in the refrigerator for 4 to 5 hr., large crystals of tetrachloroquinone formed and were removed by filtration. The filtrate was purified chromatographically on neutral alumina, the product running through the column very readily as was evident by observation under ultraviolet light. Evaporation of the eluate gave the product in fairly pure form. In a few cases recrystallization improved the purity a little.

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