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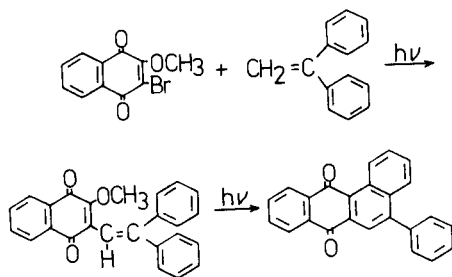
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Anthra[2,1-*b*]furan, anthra[2,1-*b*]benzo[*d*]furan, anthra[2,1-*b*]thiophene, anthra[1,2-*b*]thiophene, anthra[2,1-*b*]benzo[*d*]thiophene, anthra[2,1-*b*]pyrrole and naphtho[2,3-*c*]carbazole derivatives were synthesized in fairly good yields by a one-pot photocycloaddition reaction of 2,3-disubstituted 1,4-naphthoquinone with 1,1-diarylethylene. This is the first reported synthesis of these aromatic compounds.

J. Heterocyclic Chem., **17**, 695 (1980).

The isosteric substitution of carbon by heteroatom in biologically active polycyclic hydrocarbons provides an important class of compounds. For example, benz[*a*]acridines and benz[*c*]acridines, the heteroatom analogues of benz[*a*]anthracene, have recently been reported as carcinogens, carcinostatic agents and anti-parasitic agents (2a,b). However, the intense scrutiny of the biological effects of their analogues has been hampered because of the lack of the general synthetic routes to these heteroatom-containing polycyclic aromatic compounds.

In the previous papers (1a,b), we published that photochemical reaction of 2-bromo-3-methoxy-1,4-naphthoquinone with 1,1-diphenylethylenes gave benz[*a*]anthracene-7,12-dione derivatives in moderate to good yields, providing a simple one-pot synthetic method of the polycyclic aromatics (see Scheme 1).

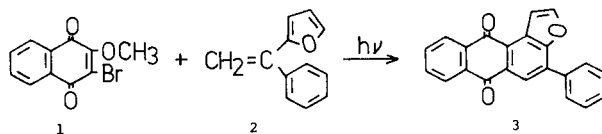


(Scheme 1)

In this report the photocycloaddition reactions were extended to the synthesis of heteroatom-containing polycyclic aromatic compounds. The following 1,1-diarylethylenes; 1-(2-furyl)-1-arylethylene, 1-(2-benzo[*b*]furyl)-1-arylethylene, 1-(2-thienyl)-1-arylethylene, 1-(3-thienyl)-1-arylethylene, 1-(2-benzo[*b*]thienyl)-1-arylethylene, 1-(2-*N*-methylpyrrolyl)-1-arylethylene and 1-(2-*N*-methylindolyl)-1-arylethylene, were examined for the reactions. Fortunately, these 1,1-diarylethylenes were all reactive for the photocycloaddition reaction. When a benzene solution (25 ml.) of 2-bromo-3-methoxy-1,4-naphthoquinone **1** (0.5 mmole) and a 1,1-diarylethylene (1 mmole) was irradiated by a high pressure mercury arc lamp (300 W), **1** disap-

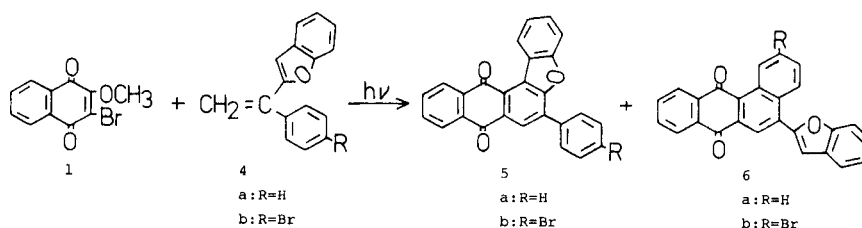
peared completely within several hours (3-10 hours) at room temperature, resulting in the formation of heteroatom-containing polycyclic aromatic *p*-quinones. Addition of pyridine in an amount equimolar to that of **1** was effective to exclude a trivial reaction leading to the formation of resinous matters.

In the absence of pyridine, 2-(2,2-diarylethenyl)-3-hydroxy-1,4-naphthoquinone was isolated as an identified product. This compound might be yielded *via* hydrolysis of 2-(2,2-diarylethenyl)-3-methoxy-1,4-naphthoquinone catalyzed by hydrogen bromide liberated during the course of the reaction. 2-(2,2-Diarylethenyl)-3-hydroxy-1,4-naphthoquinone was inert to the further photochemical reaction, resulting in the lower yield of the desired cyclization products, though its methyl ether was found to be the real intermediate for the photocyclization (7). After the complete consumption of **1**, anthra[2,1-*b*]furan-6,11-diones **3**, anthra[2,1-*b*]benzo[*d*]furan-8,13-diones **5**, anthra[2,1-*b*]thiophene-6,11-diones **8**, anthra[1,2-*b*]thiophene-6,11-diones **11**, anthra[2,1-*b*]benzo[*d*]thiophene-8,13-diones **14**, anthra[2,1-*b*]pyrrole-6,11-diones **17** or naphtho[2,3-*c*]carbazole-8,13-diones **19** were isolated in yields of 30-68%, accompanied by 5-arylbenz[*a*]anthracene-7,12-diones such as **6**, **9**, **12** or **15** (Schemes 2-8, Table 1).

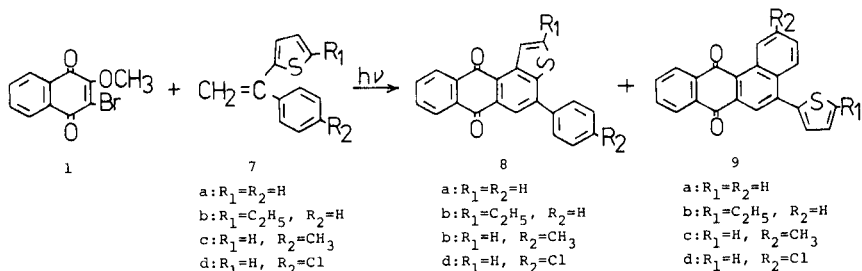


(Scheme 2)

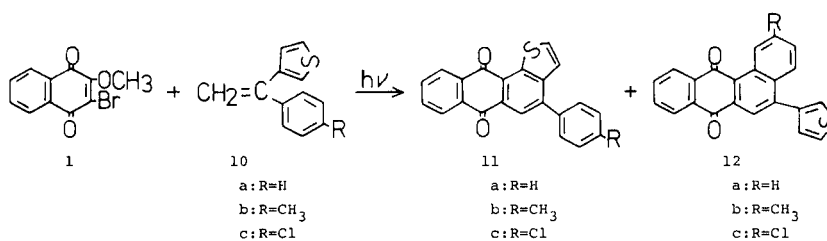
The five-membered heterocyclic ring moiety of 1,1-diarylethylene, *e.g.*, furyl, thienyl or pyrrolyl group, cyclized more favourably than the phenyl group, resulting in the formation of heteroatom-containing polycyclic aromatic *p*-quinones. However, an attempted introduction of pyridine nucleus into polycyclic aromatic compounds was not successful. 1-Phenyl-1-(3-pyridyl)ethylene or 1-phenyl-1-(4-pyridyl)ethylene afforded 5-pyridylbenz[*a*]anthracene-7,12-diones exclusively by their reaction with



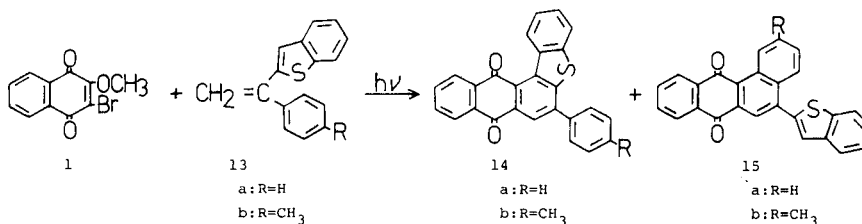
(Scheme 3)



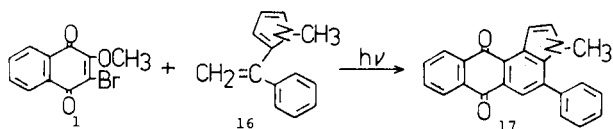
(Scheme 4)



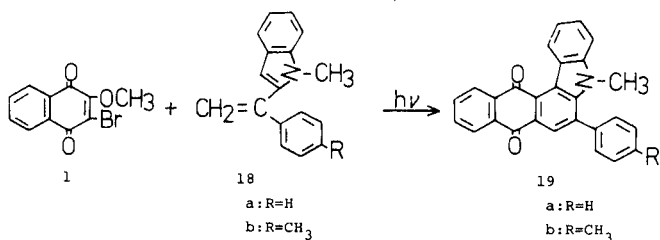
(Scheme 5)



(Scheme 6)



(Scheme 7)



(Scheme 8)

1. None of the expected anthra[1,2- α]pyridines were identified. In these 1,1-diarylethylenes, the phenyl group is much more reactive than pyridyl group in the photocyclization.

As reported previously (1b), in the similar reaction of unsymmetrically substituted 1,1-diarylethylene derivatives with 2-bromo-3-methoxy-1,4-naphthoquinone, the phenyl group with more electron-donating substituents was found to cyclize more favourably. This suggests that charge transfer type π - π -interaction between the quinone and the more electron-rich aryl of 1,1-diarylethylene may affect the product distribution of the subsequent cyclization reaction.

Table 1
Yields of Cyclized Products

1,1-Diarylethylene $\text{CH}_2=\text{C} \begin{smallmatrix} \text{Aryl}_1 \\ \text{Aryl}_2 \end{smallmatrix}$		Total Yield of Cyclized Product (%)	Cyclized Aryl (a) (Heterocyclic)	Yield (%)	Cyclized Aryl (a) (Carbocyclic)	Yield (%)
Aryl ₁ (Heterocyclic)	Aryl ₂ (Carbocyclic)					
2-Furyl	Phenyl	31	2-Furyl (3)	31	Phenyl	~0
2-Benzo[b]furyl	Phenyl	82	2-Benzo[b]furyl (5a)	30	Phenyl (6a)	52
2-Benzo[b]furyl	<i>p</i> -Bromophenyl	66	2-Benzo[b]furyl (5b)	30	<i>p</i> -Bromophenyl (6b)	36
2-Thienyl	Phenyl	70	2-Thienyl (8a)	62	Phenyl (9a)	8
2-5-Ethylthienyl	Phenyl	63	2-5-Ethylthienyl (8b)	63	Phenyl	~0
2-Thienyl	<i>p</i> -Tolyl	60	2-Thienyl (8c)	51	<i>p</i> -Tolyl (9c)	9
2-Thienyl	<i>p</i> -Chlorophenyl	46	2-Thienyl (8d)	41	<i>p</i> -Chlorophenyl (9d)	5
3-Thienyl	Phenyl	55	3-Thienyl (11a)	44	Phenyl (12a)	11
3-Thienyl	<i>p</i> -Tolyl	55	3-Thienyl (11b)	43	<i>p</i> -Tolyl (12b)	12
3-Thienyl	<i>p</i> -Chlorophenyl	51	3-Thienyl (11c)	43	<i>p</i> -Chlorophenyl (12c)	8
2-Benzo[b]thienyl	Phenyl	49	2-Benzo[b]thienyl (14a)	32	Phenyl (15a)	17
2-Benzo[b]thienyl	<i>p</i> -Tolyl	55	2-Benzo[b]thienyl (14b)	34	<i>p</i> -Tolyl (15b)	21
2- <i>N</i> -Methylpyrrolyl	Phenyl	50	2- <i>N</i> -Methylpyrrolyl (17)	50	Phenyl	~0
2- <i>N</i> -Methylindolyl	Phenyl	61	2- <i>N</i> -Methylindolyl (18a)	61	Phenyl	~0
2- <i>N</i> -Methylindolyl	<i>p</i> -Tolyl	68	2- <i>N</i> -Methylindolyl (18b)	68	<i>p</i> -Tolyl	~0
3-Pyridyl	Phenyl	60	3-Pyridyl	~0	Phenyl (22a)	60
4-Pyridyl	Phenyl	15	4-Pyridyl	~0	Phenyl (22b)	15

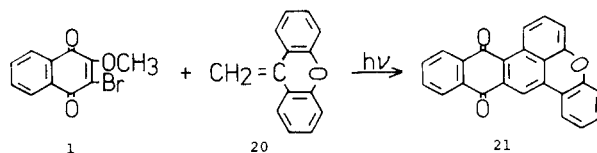
(a)The numbers in parentheses indicate the products (see text).

Thus, the product distribution in the photocycloaddition with five-membered heteroatom-containing 1,1-diarylethylenes may be explained in terms of a preferential π - π -interaction between the starting quinone and the five-membered heteroaromatic ring of 1,1-diarylethylene in the initial stages of the reaction. The electrophile can react faster, in general, with furan, thiophene or pyrrole than benzene itself. Actually, the five-membered heterocyclic aromatic ring cyclized preferentially to give photocyclized products. In contrast with these results, the poor electron distribution on pyridine nucleus may reflect the lower reactivity of pyridine ring in the photocycloaddition (*cf.* Table 1).

A similar approach to synthesize the sulfur-containing polycyclic aromatic compounds *via* the thermal Diels-Alder reaction of 1,4-naphthoquinone with 3-vinylbenzo[*b*]thiophene was once reported by Davies and Porter to yield anthra[1,2-*b*]benzo[*d*]thiophene-8,13-dione similar to 11 (3). However, those 1,1-diarylethylenes described in this report, in general, cannot be submitted to the thermal Diels-Alder reaction because of their lability against heat.

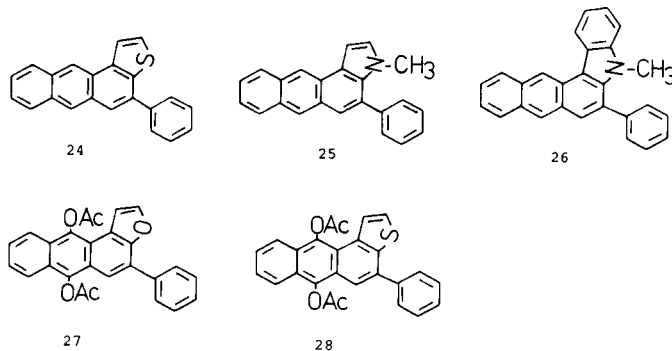
9-Methylenexanthene underwent a similar photocycloaddition reaction with 1, affording 5-oxadibenzo[*a,de*]naphthacene-9,14-dione, although the yield (4%) remains to be improved (Scheme 9).

Polycyclic aromatic *p*-quinones thus obtained were reduced by lithium aluminum hydride to the corresponding polyaromatic compounds containing heteroatom such

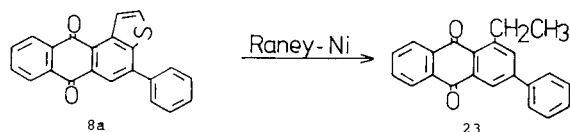


(Scheme 9)

as 24, 25 or 26. Similarly, they were reduced to the diacetate such as 27 or 28 by reductive acetylation with zinc-acetic anhydride. Desulfurization of the thiophene derivative was performed by treating with Raney-nickel (W-7) (Scheme 10).



2,3-Dihalogeno-1,4-naphthoquinone such as 2,3-dichloro- or 2,3-dibromo-1,4-naphthoquinone can also serve as starting quinone as well as 2-bromo-3-methoxy-



(Scheme 10)

1,4-naphthoquinone, although the yields of the reaction were rather poor, compared with those from **I**.

EXPERIMENTAL

Starting Materials.

The synthesis of 2-bromo-3-methoxy-1,4-naphthoquinone and 2,3-dibromo-1,4-naphthoquinone has been described in the literature (5,6). 2,3-Dichloro-1,4-naphthoquinone was commercially available and was used without further purification. 1,1-Diarylethylenes were commercially available and used after purification by distillation or recrystallization.

Photochemical Reaction.

A benzene solution (25 ml.) of a quinone (0.5 mmole) and a 1,1-diarylethylene (1 mmole) was irradiated in the presence of pyridine (0.5 mmole) with a high pressure mercury arc lamp (300W) at room temperature. After the complete consumption of the starting quinone (3-10 hours), the reaction mixture was concentrated *in vacuo*, and purified further by column chromatography on silica gel.

Physical Properties of the Photocyclization Products.

4-Phenylanthra[2,1-*b*]furan-6,11-dione (**3**).

This compound was obtained as yellow needles from methanol, m.p. 220-222° (yield 31%); nmr (deuteriochloroform): δ 6.8-8.5 ppm (11H, m), 8.47 (1H, s); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 393 nm (ϵ 7.9×10^3), 341 (sh) (5.0×10^3), 291 (3.5×10^4), 282 (sh) (3.5×10^4), 244 (2.7×10^4); ms: *m/e* 324 (M^+).

Anal. Calcd. for $\text{C}_{22}\text{H}_{12}\text{O}_3$: C, 81.47; H, 3.73. Found: C, 81.49; H, 3.99.

6-Phenylanthra[2,1-*b*]benzo[*d*]furan-8,13-dione (**5a**) and 5-(2-Benzo[*b*]furyl)benz[*a*]anthracene-7,12-dione (**6a**).

These compounds were obtained as orange crystals from chloroform-hexane-methanol, m.p. 198-199.5° (**5a**) and 264.5-265.5° (**6a**) (yield, 82% as a mixture of two isomers, **5a/6a** = 36/64); nmr (deuteriochloroform): δ 7.0-9.0 ppm (12H, m), 8.62 (1H, (**5a**), s), 8.74 (1H, (**6a**), s), 9.43 (1H, (**5a**), dd, J = 2.8 Hz), 9.80 (1H, (**6a**), d, J = 8 Hz); ir (potassium bromide): 1675 cm^{-1} ; uv (chloroform): 448 nm (ϵ 9.7×10^3), 365 (sh) (7.3×10^3), 313 (3.1×10^4), 294 (3.3×10^4), 254 (3.0×10^4), 244 (2.8×10^4); ms: *m/e* 374 (M^+).

Anal. Calcd. for $\text{C}_{26}\text{H}_{14}\text{O}_3$: C, 83.41; H, 3.77. Found: C, 83.46; H, 3.59.

6-*p*-Bromophenylanthra[2,1-*b*]benzo[*d*]furan-8,13-dione (**5b**) and 2-Bromo-5-(2-benzo[*b*]furyl)benz[*a*]anthracene-7,12-dione (**6b**).

These compounds were obtained as orange crystals, m.p. 185-195° (**5b**) and 260-265° (**6b**) (yield, 66% as a mixture of two isomers, **5b/6b** = 44/55); nmr (deuteriochloroform): δ 7.1-8.6 ppm (10H, m), 8.49 (1H, s), 8.63 (1H, s), 9.31 (1H (**5b**), d, J = 4 Hz), 9.93 (1H, (**6b**), d, J = 1 Hz); ir (potassium bromide): 1670 cm^{-1} ; ms: *m/e* 454 (M^+), 452 (M^+).

Anal. Calcd. for $\text{C}_{26}\text{H}_{13}\text{BrO}_3$: C, 68.89; H, 2.89; Br, 17.63. Found: C, 68.63; H, 2.96; Br, 17.96.

4-Phenylanthra[2,1-*b*]thiophene-6,11-dione (**8a**).

This compound was obtained as light yellow needles from chloroform-methanol, m.p. 221-221.5° (yield, 62%); nmr (deuteriochloroform): δ 7.2-8.4 ppm (9H, m), 7.78 (1H, d, J = 6 Hz), 8.27 (1H, s), 8.84 (1H, d, J = 6 Hz); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 412 nm (ϵ 4.7

$\times 10^3$), 378 (sh) (3.8×10^3), 303 (sh) (3.8×10^4), 292 (4.1×10^4), 252 (2.6×10^4); ms: *m/e* 340 (M^+).

Anal. Calcd. for $\text{C}_{22}\text{H}_{12}\text{SO}_2$: C, 77.63; H, 3.55; S, 9.42. Found: C, 77.44; H, 3.49; S, 9.42.

5-(2-Thienyl)benz[*a*]anthracene-7,12-dione (**9a**).

This compound was obtained as yellowish orange needles from chloroform-methanol, m.p. 182-183.5° (yield, 8%), nmr (deuteriochloroform): δ 7.1-8.5 ppm (10H, m), 8.34 (1H, s), 9.65 (1H, dd, J = 2.9 Hz); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 429 nm (ϵ 5.2×10^3), 345 (sh) (6.2×10^3), 292 (3.5×10^4), 248 (2.9×10^4); ms: *m/e* 340 (M^+).

Anal. Calcd. for $\text{C}_{22}\text{H}_{12}\text{SO}_2$: C, 77.63; H, 3.55. Found: C, 77.77; H, 3.39.

2-Ethyl-4-phenylanthra[2,1-*b*]thiophene-6,11-dione (**8b**).

This compound was obtained as yellow needles from chloroform, m.p. 182-185° (yield, 63%); nmr (deuteriochloroform): δ 1.40 ppm (3H, t, J = 7 Hz), 3.00 (2H, q, J = 7 Hz), 7.3-7.9 (7H, m), 8.1-8.4 (2H, m), 8.16 (1H, s), 8.51 (1H, t, J = 1 Hz); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 421 nm (ϵ 5.7×10^3), 390 (sh) (5.2×10^3), 304 (sh) (4.2×10^4), 252 (3.0×10^4).

Anal. Calcd. for $\text{C}_{24}\text{H}_{16}\text{SO}_2$: C, 78.24; H, 4.54; S, 8.70. Found: C, 78.14; H, 4.39; S, 8.91.

5-(2-5-Ethylthienyl)benz[*a*]anthracene-7,12-dione (**9b**) could not be identified from the reaction mixture.

4-*p*-Tolylanthra[2,1-*b*]thiophene-6,11-dione (**8c**).

This compound was obtained as yellow needles from benzene-methanol, m.p. 240° (yield, 51%); nmr (deuteriochloroform): δ 2.47 ppm (3H, s), 8.82 (1H, d, J = 6 Hz), 7.1-8.3 (10H, m); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 413 nm (ϵ 4.7×10^3), 381 (3.8×10^3), 306 (3.9×10^4), 294 (4.0×10^4); ms: *m/e* 354 (M^+).

Anal. Calcd. for $\text{C}_{23}\text{H}_{14}\text{SO}_2$: C, 77.94; H, 3.98; S, 9.05. Found: C, 77.73; H, 3.95; S, 9.12.

2-Methyl-5-(2-thienyl)benz[*a*]anthracene-7,12-dione (**9c**).

This compound was obtained as yellowish orange needles from benzene-methanol, m.p. 190-192° (yield, 9%); nmr (deuteriochloroform): δ 2.62 ppm (3H, s), 7.0-8.4 (10H, m), 9.55 (1H, d, J = 2 Hz); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 430 nm (ϵ 5.2×10^3), 347 (6.0×10^3), 292 (3.5×10^4), 250 (2.9×10^4); ms: *m/e* 354 (M^+).

Anal. Calcd. for $\text{C}_{23}\text{H}_{14}\text{SO}_2$: C, 77.94; H, 3.98; S, 9.05. Found: C, 77.72; H, 3.86; S, 9.23.

4-*p*-Chlorophenylanthra[2,1-*b*]thiophene-6,11-dione (**8d**).

This compound was obtained as yellow needles from benzene, m.p. 266-269° (yield, 41%); nmr (deuteriochloroform): δ 7.2-8.4 ppm (10H, m), 8.80 (1H, d, J = 6 Hz); ir (potassium bromide): 1670 cm^{-1} ; ms: *m/e* 376 (M^+), 374 (M^+).

Anal. Calcd. for $\text{C}_{22}\text{H}_{11}\text{SO}_2\text{Cl}$: C, 70.49; H, 2.96; S, 8.55; Cl, 9.46. Found: C, 70.65; H, 2.90; S, 8.69; Cl, 9.26.

2-Chloro-5-(2-thienyl)benz[*a*]anthracene-7,12-dione (**9d**).

This compound was obtained as orange needles from benzene, m.p. 235-237° (yield, 5%); nmr (deuteriochloroform): δ 7.1-8.4 ppm (10H, m), 9.65 (1H, d, J = 2 Hz); ir (potassium bromide): 1670 cm^{-1} ; ms: *m/e* 376 (M^+), 374 (M^+).

4-Phenylanthra[1,2-*b*]thiophene-6,11-dione (**11a**).

This compound was obtained as yellow needles from benzene-methanol, m.p. 231-232° (yield, 44%); nmr (deuteriochloroform): δ 7.1-8.4 ppm (12H, m); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 410 nm (ϵ 4.5×10^3), 375 (3.5×10^3), 305 (3.5×10^4), 250 (3.2×10^4); ms: *m/e* 340 (M^+).

Anal. Calcd. for $\text{C}_{22}\text{H}_{12}\text{SO}_2$: C, 77.63; H, 3.55; S, 9.42. Found: C, 77.49; H, 3.57; S, 9.58.

5-(3-Thienyl)benz[*a*]anthracene-7,12-dione (**12a**).

This compound was obtained as orange needles from chloroform-methanol, m.p. 193-194° (yield, 11%); nmr (deuteriochloroform): δ 7.1-8.4 ppm (11H, m), 9.40 (1H, d, $J = 2$ Hz); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 425 nm ($\epsilon 4.0 \times 10^3$), 340 (5.6×10^3), 285 (2.8×10^4), 250 (3.3×10^4); ms: m/e 340 (M^+).

Anal. Calcd. for $C_{22}H_{12}SO_2$: C, 77.63; H, 3.55; S, 9.42. Found: C, 77.44; H, 3.54; S, 9.28.

4-*p*-Tolylanthra[1,2-*b*]thiophene-6,11-dione (**11b**).

This compound was obtained as yellow needles from chloroform-methanol, m.p. 251-252.5° (yield, 43%); nmr (deuteriochloroform): δ 2.48 ppm (3H, s), 7.1-8.3 (11H, m); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 429 nm ($\epsilon 2.8 \times 10^3$), 351 (5.0×10^3), 288 (3.4×10^4), 255 (3.5×10^4); ms: m/e 354 (M^+).

Anal. Calcd. for $C_{23}H_{14}SO_2$: C, 77.94; H, 3.98; S, 9.05. Found: C, 77.73; H, 3.95; S, 9.19.

2-Methyl-5-(3-thienyl)benz[*a*]anthracene-7,12-dione (**12b**).

This compound was obtained as orange needles from chloroform-methanol, m.p. 201-203° (yield, 12%); nmr (deuteriochloroform): δ 2.62 ppm (3H, s), 7.1-8.3 (10H, m), 9.54 (1H, s); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 435 nm ($\epsilon 3.0 \times 10^3$), 345 (5.0×10^3), 295 (3.2×10^4), 253 (2.5×10^4); ms: m/e 354 (M^+).

4-*p*-Chlorophenylanthra[1,2-*b*]thiophene-6,11-dione (**11c**).

This compound was obtained as yellow needles from benzene, m.p. 282-283° (yield, 43%); nmr (deuteriochloroform): δ 7.1-8.4 ppm (11H, m); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 432 nm ($\epsilon 3.0 \times 10^3$), 353 (6.0×10^3), 292 (3.2×10^4), 258 (3.2×10^4); ms: m/e 376 (M^+), 374 (M^+).

Anal. Calcd. for $C_{22}H_{11}SO_2Cl$: C, 70.49; H, 2.96; S, 8.55; Cl, 9.46. Found: C, 70.25; H, 2.87; S, 8.69; Cl, 9.45.

2-Chloro-5-(3-thienyl)benz[*a*]anthracene-7,12-dione (**12c**).

This compound was obtained as orange needles from benzene, m.p. 235-236° (yield, 8%); nmr (deuteriochloroform): δ 7.1-8.4 ppm (10H, m), 9.60 (1H, s); ir (potassium bromide): 1670 cm^{-1} ; ms: m/e 376 (M^+), 374 (M^+).

Anal. Calcd. for $C_{22}H_{11}SO_2Cl$: C, 70.49; H, 2.96; S, 8.55; Cl, 9.46. Found: 70.23; H, 2.95; S, 8.36; Cl, 9.35.

6-Phenylanthra[2,1-*b*]benzo[*d*]thiophene-8,13-dione (**14a**).

This compound was obtained as yellow needles from benzene, m.p. 226-227° (yield, 32%); nmr (deuteriochloroform): δ 7.2-8.4 ppm (13H, m), 8.90 (1H, dd, $J = 4.8$ Hz); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 410 nm ($\epsilon 2.6 \times 10^3$), 336 (1.6×10^4), 325 (1.8×10^4), 252 (2.0×10^4); ms: m/e 390 (M^+).

Anal. Calcd. for $C_{26}H_{14}SO_2$: C, 79.98; H, 3.61; S, 8.21. Found: C, 79.85; H, 3.65; S, 8.45.

5-(2-Benzo[*b*]thienyl)benz[*a*]anthracene-7,12-dione (**15a**).

This compound was obtained as orange needles from benzene, m.p. 183-185° (yield, 17%); nmr (deuteriochloroform): δ 7.1-8.5 ppm (13H, m), 9.85 (1H, dd, $J = 2.10$ Hz); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 368 nm ($\epsilon 4.5 \times 10^3$), 321 (1.4×10^4), 285 (1.6×10^4), 254 (2.1×10^4); ms: m/e 390 (M^+).

6-*p*-Tolylanthra[2,1-*b*]benzo[*d*]thiophene-8,13-dione (**14b**).

This compound was obtained as yellow needles from benzene, m.p. 230-231° (yield, 34%); nmr (deuteriochloroform): δ 2.48 ppm (3H, s), 7.1-8.3 (12H, m), 8.85 (1H, m); ms: m/e 404 (M^+).

Anal. Calcd. for $C_{27}H_{16}SO_2$: C, 80.17; H, 3.99; S, 7.93. Found: C, 80.10; H, 3.85; S, 8.08.

2-Methyl-5-(2-benzo[*b*]thienyl)benz[*a*]anthracene-7,12-dione (**15b**).

This compound was obtained as orange needles from benzene, m.p. 187-188° (yield, 21%); nmr (deuteriochloroform): δ 2.65 ppm (3H, s),

7.1-8.4 (12H, m), 9.60 (1H, d, $J = 2$ Hz); ir (potassium bromide): 1670 cm^{-1} ; ms: m/e 404 (M^+).

3-Methyl-4-phenylanthra[2,1-*b*]pyrrole-6,11-dione (**17**).

This compound was obtained as orange yellow prisms from chloroform, m.p. 240° (yield, 50%); nmr (deuteriochloroform): δ 3.32 ppm (3H, s), 7.20 (1H, d, $J = 2$ Hz), 7.4 (5H, br s), 7.71 (1H, d, $J = 2$ Hz), 7.5-7.9 (2H, m), 7.93 (1H, s), 8.0-8.4 (2H, m); ir (potassium bromide): 1665 cm^{-1} ; uv (chloroform): 440 nm (sh) ($\epsilon 4.1 \times 10^3$), 420 (sh) (4.4×10^3), 392 (5.0×10^3), 306 (sh) (2.7×10^4), 291 (3.2×10^4), 250 (3.0×10^4), 247 (sh) (2.9×10^4); ms: m/e 337 (M^+).

Anal. Calcd. for $C_{23}H_{15}NO_2$: C, 81.88; H, 4.48; N, 4.15. Found: C, 81.67; H, 4.37; N, 4.18.

5-Methyl-6-phenylanthro[2,3-*c*]carbazole-8,13-dione (**19a**).

This compound was obtained as orange prisms from chloroform-hexane, m.p. 256-257.5° (yield, 61%); nmr (deuteriochloroform): δ 3.13 ppm (3H, s), 6.9-7.8 (5H, m), 7.4 (5H, br s), 7.9-8.3 (2H, m), 8.19 (1H, s), 9.36 (1H, d, $J = 8$ Hz); ir (potassium bromide): 1675, 1645 cm^{-1} ; uv (chloroform): 440 nm ($\epsilon 5.7 \times 10^3$), 417 (6.4×10^3), 344 (2.7×10^4), 332 (sh) (2.4×10^4), 303 (1.7×10^4), 268 (3.2×10^4), 246 (4.0×10^4); ms: m/e 387 (M^+).

Anal. Calcd. for $C_{27}H_{17}NO_2$: C, 83.70; H, 4.42; N, 3.62. Found: C, 83.41; H, 4.63; N, 3.45.

5-Methyl-6-*p*-tolylanthro[2,3-*c*]carbazole-8,13-dione (**19b**).

This compound was obtained as orange prisms from chloroform-hexane, m.p. 286.5-287.5° (yield, 68%); nmr (deuteriochloroform): δ 2.46 ppm (3H, s), 3.36 (3H, s), 7.1-7.8 (9H, m), 8.21 (1H, s), 8.0-8.4 (2H, m), 9.38 (1H, d, $J = 8$ Hz); ms: m/e 401 (M^+).

Anal. Calcd. for $C_{28}H_{19}NO_2$: C, 83.77; H, 4.77; N, 3.49. Found: C, 83.55; H, 4.63; N, 3.59.

5-(3-Pyridyl)benz[*a*]anthracene-7,12-dione (**22a**).

This compound was obtained as yellow crystals from benzene m.p. 116-120° (yield, 60%); nmr (deuteriochloroform): δ 7.4-8.5 ppm (12H, m), 9.88 (1H, dd, $J = 2.10$ Hz); ir (potassium bromide): 1660 cm^{-1} ; ms: m/e 335 (M^+).

5-(4-Pyridyl)benz[*a*]anthracene-7,12-dione (**22b**).

This compound was obtained as yellow needles from ethanol, m.p. 232-234° (yield, 15%); nmr (deuteriochloroform): δ 7.1-8.5 ppm (12H, m), 9.45 (1H, dd, $J = 2.8$ Hz); ir (potassium bromide): 1670 cm^{-1} ; ms: m/e 335 (M^+).

Anal. Calcd. for $C_{23}H_{13}NO_2$: C, 82.37; H, 3.91; N, 4.18. Found: C, 82.15; H, 3.93; N, 4.36.

5-Oxadibenzo[*a,d*]naphthacene-9,14-dione (**21**).

This compound was obtained as purple needles from chloroform-hexane, m.p. 275-276° (yield, 4%); nmr (deuteriochloroform): δ 6.7-8.4 ppm (10H, m), 8.33 (1H, s), 9.22 (1H, d, $J = 8$ Hz); ir (potassium bromide): 1670 cm^{-1} ; uv (chloroform): 530 nm ($\epsilon 6.6 \times 10^3$), 391 (9.7×10^3), 373 (6.0×10^3), 327 (3.0×10^4), 319 (sh) (2.8×10^4), 305 (sh) (2.2×10^4), 242 (2.2×10^4).

Anal. Calcd. for $C_{24}H_{12}O_3$: C, 82.75; H, 3.42. Found: C, 82.96; H, 3.31.

Reduction of the Photo-Products to the Corresponding Polycyclic Aromatic Compounds.

A tetrahydrofuran solution (50 ml.) of *p*-quinone (0.05 mmole) and an excess amount (*ca.* 3 equivalents) of lithium aluminum hydride was refluxed for 8 hours. After hydrolysis of an excess lithium aluminum hydride the reaction mixture was purified by column chromatography on silica gel.

Physical Properties of the Polycyclic Aromatic Compounds.

4-Phenylanthra[2,1-*b*]thiophene (**24**).

This compound was obtained as pale yellow crystals from chloroform-methanol, m.p. 155.5-157° (yield, 32%); nmr (deuteriochloroform): δ

7.1-8.4 ppm (12H, m), 8.42 (1H, s), 8.77 (1H, s); ir (potassium bromide): neither CO nor OH; uv (chloroform): 388 nm (ϵ 8.8×10^3), 368 (1.2×10^4), 350 (8.8×10^3), 337 (sh) (5.5×10^3), 293 (6.9×10^4), 284 (sh) (5.9×10^4), 271 (5.5×10^4), 256 (sh) (4.2×10^4), 248 (sh) (3.8×10^4); ms: m/e 310 (M^+).

3-Methyl-4-phenylanthra[2,1-b]pyrrole (25).

This compound was obtained as pale yellow crystals, m.p. 146.5-147° (yield, 52%); nmr (deuteriochloroform): δ 3.19 ppm (3H, s), 6.79 (1H, d, J = 2 Hz), 7.05 (1H, d, J = 2 Hz), 6.7-8.0 (9H, m), 7.83 (1H, s), 8.16 (1H, s), 8.53 (1H, s); ir (potassium bromide): neither CO nor OH; uv (ethanol): 396 nm (ϵ 6.3×10^3), 376 (8.1×10^3), 360 (sh) (6.2×10^3), 302 (sh) (3.0×10^4), 288 (4.9×10^4), 271 (5.6×10^4), 237 (4.3×10^4), 223 (sh) (3.2×10^4), 207 (2.9×10^4); ms: m/e 307 (M^+).

Anal. Calcd. for $C_{23}H_{17}N$: C, 89.86; H, 5.58; N, 4.56. Found: C, 89.98; H, 5.50; N, 4.61.

5-Methyl-6-phenylanthro[2,3-c]carbazole (26).

This compound was obtained as pale green crystals, m.p. 189.5-191° (yield, 47%); nmr (deuteriochloroform): δ 3.40 ppm (3H, s), 6.7-8.7 (13H, m), 7.65 (1H, s), 8.30 (1H, s), 9.09 (1H, s); ir (potassium bromide): neither CO nor OH; uv (ethanol): 427 nm (ϵ 4.4×10^3), 403 (5.3×10^3), 377 (1.2×10^4), 358 (8.3×10^3), 341 (4.9×10^4), 310 (3.3×10^4), 290 (5.2×10^4), 265 (4.8×10^4), 260 (sh) (4.7×10^4), 251 (sh) (4.2×10^4), 232 (3.5×10^4), 219 (4.7×10^4), 205 (5.1×10^4); ms: m/e 357 (M^+).

Anal. Calcd. for $C_{27}H_{19}N$: C, 90.72; H, 5.36; N, 3.29. Found: C, 90.43; H, 5.23; N, 3.82.

Reductive Acetylation of the Photo-Products.

p-Quinone (0.1 mmole) and an excess amount of zinc powder were added to acetic anhydride (10 ml.). Then, the reaction mixture was refluxed for 30 minutes. After the yellow color due to the *p*-quinone disappeared completely, the reaction mixture was hydrolyzed and neutralized with sodium carbonate. The diacetate was extracted with ether from the reaction mixture and purified further by column chromatography on silica gel.

Physical Properties of the Diacetate.

6,11-Diacetoxy-4-phenylanthra[2,1-b]furan (27).

This compound was obtained as pale yellow crystals, m.p. 261.5-264° (yield, 79%); nmr (deuteriochloroform): δ 2.62 ppm (3H, s), 2.66 (3H, s), 7.1-8.0 (12H, m); ir (potassium bromide): 1765 cm^{-1} ; ms: m/e (relative intensity) 410 (M^+ , 19), 368 ($M^+ - 42$, 44), 326 ($M^+ - 84$, 100).

6,11-Diacetoxy-4-phenylanthra[2,1-b]thiophene (28).

This compound was obtained as pale yellow crystals, m.p. 263-264° (yield, 60%); nmr (deuteriochloroform): δ 2.61 ppm (3H, s), 2.69 (3H, s), 7.1-8.0 (11H, m), 8.24 (1H, d, J = 6 Hz); ir (potassium bromide): 1775 cm^{-1} ; uv (chloroform): 402 nm (ϵ 1.2×10^4), 380 (1.4×10^4), 362 (1.1×10^4), 345 (sh) (7.1×10^3), 297 (6.8×10^4), 275 (sh) (4.0×10^4), 246 (sh) (3.5×10^4); ms: m/e (relative intensity) 426 (M^+ , 23), 384 ($M^+ - 42$, 41), 342 ($M^+ - 84$, 100).

Anal. Calcd. for $C_{26}H_{18}SO_4$: C, 73.22; H, 4.25; S, 7.52. Found: C, 73.15; H, 4.54; S, 7.71.

Reductive Desulfurization of 4-Phenylanthra[2,1-b]thiophene-6,11-dione (8a).

Raney nickel (W-7) was prepared by the method of Adkins (4). A benzene solution (10 ml.) of 8a (0.3 mmole) was added to the ethereal suspension (20 ml.) of Raney nickel (W-7) which was prepared from one gram of nickel-aluminum alloy. After refluxing for 4 hours, the reaction mixture was worked-up as usual and was purified further by column chromatography on silica gel.

1-Ethyl-3-phenylanthracene-9,10-dione (23).

This compound was obtained as yellow needles from chloroform-methanol, m.p. 133-134.5° (yield, 13%); nmr (deuteriochloroform): δ 1.38 ppm (3H, t, J = 8 Hz), 2.88 (2H, q, J = 8 Hz), 7.1-8.6 (11H, m); ir (potassium bromide): 1650 cm^{-1} ; uv (chloroform): 435 nm (sh) (ϵ 7.3×10^3), 315 (3.3×10^3), 263 (3.9×10^4); ms: m/e 312 (M^+).

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