

(lit.<sup>13</sup> m.p. 148–150°). The mother liquor was evaporated to dryness, affording 5.6 g. of a dark oil which was distilled at 96–102° (0.1 mm.) to produce 2.93 g. (27%) of an oil which did not crystallize (lit.<sup>6</sup> m.p. 40–41°). An infrared spectrum of this material (CHCl<sub>3</sub>) was identical with one of an authentic sample of *cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-one.<sup>6</sup> The compound formed a 2,4-dinitrophenylhydrazone, m.p. 195–197° (lit.<sup>6</sup> m.p. 195–196.5°).

**B. From Fluoren-9-ol.**—Fluoren-9-ol<sup>13</sup> (5.2 g., 0.03 mole) was reduced by the procedure described in A. After evaporation of the methylamine at room temperature, 25 ml. of water was added, and the resulting mixture was extracted with ether. On evaporation of the ether, 3.56 g. (64%) of a liquid remained, which crystallized to a soft yellow solid and which formed a 2,4-dinitrophenylhydrazone, m.p. 195–197°. An infrared spectrum of the product of the reaction was identical with that of the product of A.

(13) A. A. R. Sayigh, *J. Org. Chem.*, **25**, 1707 (1960).

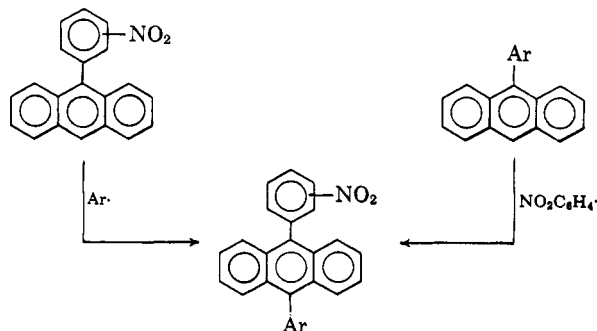
### Homolytic Aromatic Substitution. IV.<sup>1</sup> Synthesis of 9-Aryl-10-nitrophenylanthracenes

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In an earlier paper of this series Meerwein arylation of anthracene was shown to afford a general route to 9-aryl- and 9,10-diarylanthracenes and, more importantly, to otherwise inaccessible nitrophenyl- and dinitrophenylanthracenes.<sup>1</sup> This reaction has now been employed to prepare previously unknown 9-aryl-10-nitrophenylanthracenes. All of these compounds are unsymmetrically substituted derivatives of 9,10-diphenylanthracene and possess a common structural feature, a nitrophenyl group. Obviously, it is possible to envisage alternative routes to such compounds as indicated in the accompanying equations. For example, 9-phenyl-10-*o*-nitrophenylanthracene is the major product expected from homolytic phenylation of 9-*o*-nitrophenylanthracene as well as by *o*-nitrophenylation of 9-phenylanthracene. Preparation of a compound by the two methods establishes constitution provided that the identities of the starting materials are known. 9-Nitrophenylanthracenes (*ortho*, *meta*, and *para*) were available by Meerwein arylation of anthracene<sup>1</sup> and the additional 9-arylanthracenes were synthesized by unequivocal methods.



(1) Part III may be consulted for historical introduction and discussion of mechanism: S. C. Dickerman, A. M. Felix, and L. B. Levy, *J. Org. Chem.*, **29**, 26 (1964).

The 9-aryl-10-nitrophenylanthracenes described here are listed in Table I which also includes yields, melting points, and elemental analyses. Several of these derivatives of 9,10-diphenylanthracene (**3**, **4**, **7**, and **9**) have been reported in the previous paper<sup>1</sup> and are included in Table I to facilitate comparison. The present study completes three sets of constitutional isomers: the 9-phenyl-10-nitrophenylanthracenes (**1–3**), the 9-nitrophenyl-10-nitrophenylanthracenes (**4–9**), and the 9-methoxyphenyl-10-nitrophenylanthracenes (**10–18**). Comparison of infrared spectra and mixture melting points served to establish the identity of samples prepared by alternative routes. Six of the 9-methoxyphenyl-10-nitrophenylanthracenes were synthesized from 9-methoxyphenylanthracenes only and the assignment of constitution to these compounds was made on the basis of spectra and by analogy.

Comparison of yields of a given compound by alternative syntheses (Table I) is revealing. Methoxyphenylation is a generally less efficient route than nitrophenylation and, in a particular instance, *o*-methoxyphenylation of 9-*p*-nitrophenylanthracene failed to yield the desired compound. Since homolytic *o*-methoxyphenylation of naphthalene has been observed,<sup>2</sup> failure here may be ascribed to one or more competing reactions, for example, abstraction from acetone and the Sandmeyer reaction.<sup>1</sup>

The ultraviolet absorption spectra of nineteen derivatives of 9,10-diphenylanthracene have been measured and the data for these compounds together with those for the parent hydrocarbon are recorded in Table II. Significantly, except for the disappearance of a shoulder in all compounds that possess a *p*-nitro group, the absorption maxima and extinction coefficients are essentially indistinguishable from those of 9,10-diphenylanthracene. In other words the red shifts in the longest wavelength absorption bands in anthracene, that result from substitution of phenyl groups at the 9,10-positions, are independent of the nature and position of substituents in the phenyl groups. Various interpretations of this type of bathochromic shift have been discussed.<sup>3,4</sup>

#### Experimental<sup>5</sup>

**9-*o*-Methoxyphenylanthracene.**—A solution of 17.5 g. (0.09 mole) of 9-anthrone in 200 ml. of warm benzene was added over a period of 15 min. to an ether solution of *o*-methoxyphenyllithium prepared from 21.5 g. (0.115 mole) of *o*-bromoanisole and 1.60 g. (0.225 g.-atom) of lithium. After the mixture had been stirred at 40–45° for 1 hr. it was poured into a mixture of ice and concentrated hydrochloric acid. The organic phase was separated, dried, and concentrated. The viscous residue was extracted with boiling ethanol to yield 10.5 g. (41%) of product. The analytical sample was recrystallized from benzene–hexane and melted at 176–177°:  $\lambda_{\text{max}}^{\text{ethanol}}$   $\mu\text{m}$  (log  $\epsilon$ ), 255 (4.93), 346 (3.83), 364 (4.03), and 384 (4.00).

*Anal.* Calcd. for C<sub>21</sub>H<sub>16</sub>O: C, 88.70; H, 5.67; mol. wt., 284. Found: C, 88.91; H, 5.73; mol. wt., 292.

**9-*m*-Methoxyphenylanthracene.**—The required Grignard reagent was prepared under nitrogen in tetrahydrofuran from 2.8 g. (0.12 g.-atom) of magnesium and 22.0 g. (0.12 mole) of *m*-

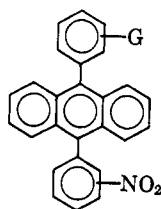
(2) P. S. Johnson and W. A. Waters, *J. Chem. Soc.*, 4652 (1962).

(3) H. H. Jaffe and M. Orchin, "Theory and Applications of Electronic Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 15.

(4) H. H. Jaffe and O. Chalvet, *J. Am. Chem. Soc.*, **85**, 1561 (1963).

(5) Melting points above 250° were taken on a Mel-Temp apparatus. Ultraviolet spectra were determined with a Cary Model 15 spectrophotometer. Infrared spectra were taken with a Baird Model 4-55 spectrophotometer using potassium bromide wafers. Analyses were performed by the Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y.

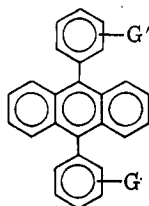
TABLE I. 9-ARYL-10-NITROPHENYLANTHRACENES



Compd.	G	NO <sub>2</sub>	Syntheses and yields <sup>a</sup>		M.p., °C.	Formula	% C	% H	% N
			Aniline, %	Nitroaniline, %					
1	H	<i>o</i>	30 <sup>b</sup>	<i>o</i> , 29 <sup>b</sup>	301-302	C <sub>26</sub> H <sub>17</sub> NO <sub>2</sub>	Calcd. 83.18	4.56	3.73
2		<i>m</i>	27 <sup>b</sup>	<i>m</i> , 26 <sup>e</sup>	245-246		Found 83.11	4.56	3.62
3 <sup>d</sup>		<i>p</i>		<i>p</i> , 40 <sup>b</sup>	296-297		Found 83.16	4.66	3.50
4	NO <sub>2</sub>	<i>o</i>		<i>o</i> , 33 <sup>b</sup>	392-393 <sup>e</sup>	C <sub>26</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	Calcd. 74.28	3.84	6.66
5		<i>o</i>	<i>o</i> -NO <sub>2</sub> , 16 <sup>b</sup>	<i>m</i> , 23 <sup>b</sup>	244-246		Found 74.73	4.26	6.41
6		<i>o</i>	<i>o</i> -NO <sub>2</sub> , 20	<i>p</i> , 32	337-338		Found 74.94	4.21	6.61
7 <sup>d</sup>		<i>m</i>			344-345				
8		<i>m</i>	<i>m</i> -NO <sub>2</sub> , 34	<i>p</i> , 35	354-356		Found 74.76	4.11	6.40
9 <sup>d</sup>		<i>p</i>			>400 dec.				
10	OCH <sub>3</sub>	<i>o</i>		<i>o</i> , 23	289-290 <sup>e</sup>	C <sub>27</sub> H <sub>19</sub> NO <sub>3</sub>	Calcd. 79.98	4.72	3.45
11		<i>o</i>	<i>m</i> -OCH <sub>3</sub> , 15 <sup>c</sup>	<i>o</i> , 22	217-218		Found 80.31	4.98	3.64
12		<i>o</i>		<i>o</i> , 29	322-323		Found 80.11	4.97	3.70
13		<i>m</i>		<i>m</i> , 21	203-204		Found 80.15	4.68	3.51
14		<i>m</i>		<i>m</i> , 30	210-211		Found 80.26	4.98	3.52
15		<i>m</i>		<i>m</i> , 40	253-254		Found 80.00	4.88	3.41
16		<i>p</i>	<i>o</i> -OCH <sub>3</sub> , 0 <sup>c</sup>	<i>p</i> , 36	258-259		Found 80.53	4.94	3.67
17		<i>p</i>	<i>m</i> -OCH <sub>3</sub> , 21 <sup>c</sup>	<i>p</i> , 34	233-234		Found 80.43	4.94	3.64
18		<i>p</i>	<i>p</i> -OCH <sub>3</sub> , 15 <sup>c</sup>	<i>p</i> , 49	315-316		Found 80.03	4.75	3.54
19	Cl	<i>p</i>	<i>p</i> -Cl, 32 <sup>b</sup>	<i>p</i> , 44 <sup>b</sup>	384-385 dec.	C <sub>26</sub> H <sub>16</sub> ClNO <sub>2</sub> <sup>f</sup>	Calcd. 76.19	3.93	3.42
							Found 76.44	4.12	3.24

<sup>a</sup> Based on 9-arylanthracene and with 5 equiv. of diazonium salt unless otherwise specified. <sup>b</sup> Yield with 7.5 equiv. <sup>c</sup> Yield with 10 equiv. <sup>d</sup> Previously described. <sup>e</sup> The configuration of the isolated compound has not been established. <sup>f</sup> Cl: calcd., 8.65; found, 8.63.

TABLE II. ULTRAVIOLET SPECTRA OF 9-ARYL'-10-ARYLANTHRACENES



Compd.	G'	G	Absorption maxima in $\mu$ (log $\epsilon$ ) <sup>a,b</sup>						
			256	262 (5.02)	323 (3.19)	340 (3.54)	358 (3.88)	376 (4.09)	396 (4.11)
1	H	H							
2	H	NO <sub>2</sub>	254 (4.90)	261 (5.07)	324 (3.32)	340 (3.62)	357 (3.90)	376 (4.08)	396 (4.03)
3		<i>p</i>	254 (4.89)	261 (5.09)	322 (3.16)	340 (3.56)	357 (3.90)	375 (4.10)	395 (4.07)
4	NO <sub>2</sub>	NO <sub>2</sub>	259 (5.07)	259 (5.07)	322 (3.46)	339 (3.61)	357 (3.89)	375 (4.07)	395 (4.08)
5		<i>o</i>	251 (4.90)	260 (5.09)	322 (3.37)	340 (3.64)	357 (3.90)	376 (4.04)	396 (3.99)
6		<i>o</i>	252 (4.96)	260 (5.15)	322 (3.28)	339 (3.64)	357 (3.92)	375 (4.11)	395 (4.04)
7		<i>o</i>		258 (4.96)	322 (3.36)	339 (3.62)	357 (3.87)	376 (4.04)	396 (4.04)
8		<i>m</i>	251 (4.99)	259 (5.22)	320 (3.46)	338 (3.68)	356 (3.95)	375 (4.10)	395 (4.10)
9		<i>m</i>		259 (5.12)	323 (3.43)	339 (3.65)	357 (3.90)	375 (4.08)	394 (4.09)
10		<i>p</i>		256 (5.05)	322 (3.44)	339 (3.62)	357 (3.87)	376 (4.07)	395 (4.10)
11	OCH <sub>3</sub>	NO <sub>2</sub>							
12		<i>o</i>	253 (4.84)	261 (5.05)	323 (3.22)	340 (3.56)	357 (3.86)	376 (4.04)	396 (4.00)
13		<i>o</i>	253 (4.90)	261 (5.08)	323 (3.28)	340 (3.62)	358 (3.91)	377 (4.08)	396 (4.05)
14		<i>o</i>	254 (4.81)	262 (5.04)	323 (3.13)	341 (3.55)	358 (3.85)	377 (4.04)	397 (4.00)
15		<i>m</i>	253 (4.95)	261 (5.16)	322 (3.24)	339 (3.61)	357 (3.93)	375 (4.13)	396 (4.10)
16		<i>m</i>	253 (4.96)	260 (5.06)	323 (3.28)	339 (3.61)	357 (3.92)	375 (4.11)	396 (4.08)
17		<i>m</i>	253 (4.87)	261 (5.10)	322 (3.17)	340 (3.56)	358 (3.89)	376 (4.09)	396 (4.06)
18		<i>p</i>		260 (5.07)	321 (3.21)	339 (3.55)	357 (3.86)	375 (4.05)	395 (4.06)
19		<i>p</i>		260 (5.09)	323 (3.28)	340 (3.60)	357 (3.88)	375 (4.08)	395 (4.08)
20		<i>p</i>		261 (4.98)	324 (3.29)	340 (3.54)	358 (3.83)	376 (4.01)	396 (4.02)
21	<i>p</i> -Cl	<i>p</i>		258 (5.00)	323 (3.35)	340 (3.61)	357 (3.88)	375 (4.07)	395 (4.08)

<sup>a</sup> In methylene chloride. <sup>b</sup> The reported maxima at 251-254, 321-324, and 338-341  $m\mu$  represent shoulders.

bromoanisole. To this solution was added 21.0 g. (0.11 mole) of 9-anthrone in 100 ml. of tetrahydrofuran. After stirring for 45 min., the mixture was poured into ice-concentrated hydrochloric acid. The organic products were extracted with benzene and the extracts were dried over sodium sulfate. Evaporation of the benzene left an oily residue that was chromatographed on alumina in 3:2 benzene-hexane. The blue-fluorescing band was collected and recrystallized from aqueous ethanol to yield 7.4 g. (24%) of pale yellow product: m.p. 113.5–114.5°;  $\lambda_{\text{max}}^{\text{ethanol}}$  m $\mu$  (log  $\epsilon$ ), 254 (5.16), 346 (3.99), 364 (4.03), and 384 (3.83).

Anal. Calcd. for  $\text{C}_{21}\text{H}_{16}\text{O}$ : C, 88.70; H, 5.67. Found: C, 88.63; H, 5.67.

**General Procedure for Preparation of 9-Methoxyphenyl-10-nitrophenylanthracenes.**—A solution of 1.42 g. (5.0 mmoles) of a 9-methoxyphenylanthracene<sup>7</sup> and 0.83 g. (5.0 moles) of cupric chloride dihydrate in 240 ml. of acetone was added to a three-necked flask fitted with dropping funnel, condenser, and mechanical stirrer. The system was flushed with nitrogen and to the flask was added 60 ml. of an aqueous solution of a nitrobenzenediazonium chloride, prepared from 3.45 g. (25 mmoles) of nitroaniline, 12 ml. of 6 N hydrochloric acid, 1.73 g. (25 mmoles) of sodium nitrite, and diluted with water to volume. After stirring for about 1 hr. (9-*o*-nitrophenyl- and 9-*p*-nitrophenyl-10-*p*-methoxyphenylanthracene crystallize from reaction mixtures and may be isolated by filtration), the reaction mixture was poured into 500 ml. of water and the organic products were extracted with three 50-ml. portions of benzene. The combined extracts were washed with 20% aqueous sodium hydroxide and with water. After drying over sodium sulfate, the benzene was removed under reduced pressure and codistillation with ethylene glycol was employed to remove nitrochlorobenzene. The distillate was discarded and the ethylene glycol solution of the nonvolatile fraction was diluted with water and gave a viscous oil that was dissolved in benzene. After drying over anhydrous sodium sulfate, the benzene was removed under reduced pressure. Chromatography of the residue in 2:1 benzene-hexane on 100 g. of neutral alumina (Merck) gave 9-methoxyphenylanthracene followed by a yellow band of 9-methoxyphenyl-10-nitrophenylanthracene. The yellow products were recrystallized from benzene-ethanol or benzene-hexane. Yields, melting points, and elemental analyses of the nine constitutional isomers are listed in Table I and the ultraviolet spectra are recorded in Table II.

The three reverse syntheses from diazotized anisidines and 9-nitrophenylanthracenes<sup>1</sup> were accomplished as described above except that 10 equiv. of diazonium salt was used and the reactions were continued for 2 hr. The yields are recorded in Table I.

**General Procedure for Preparation of 9-Phenyl- and 9-Nitrophenyl-10-nitrophenylanthracenes.**—A solution of 0.254 g. (1 mmole) of 9-phenylanthracene or 0.299 g. (1 mmole) of 9-nitrophenylanthracene<sup>1</sup> and 0.170 g. (1 mmole) of cupric chloride dihydrate in 40 ml. of acetone was placed in a three-necked flask fitted with a stirrer, condenser, and addition funnel. The apparatus and contents were flushed with nitrogen and to the flask was added with stirring 10 ml. of an aqueous solution of nitrobenzenediazonium chloride that had been prepared from 1.04 g. (7.5 mmoles) of nitroaniline, 1.87 ml. of concentrated hydrochloric acid, diluted with 1.5 ml. of water, and 0.569 g. (8.2 mmoles) of sodium nitrite. The excess nitrous acid was destroyed with sulfamic acid and the solution was diluted to volume with water. After addition of the solution of diazonium chloride, the stirring was continued for 30 min. and the reaction mixture was refrigerated overnight. 9-Phenyl-10-*p*-nitrophenylanthracene, 9-phenyl-10-*o*-nitrophenylanthracene, 9-*o*-nitrophenyl-10-*p*-nitrophenylanthracene, and 9-*m*-nitrophenyl-10-*p*-nitrophenylanthracene usually crystallized from the respective reaction mixtures and were isolated by filtration. In the event that precipitation did not occur, the reaction mixture was steam distilled and the distillate was discarded. The nonvolatile residue was dissolved in benzene and the benzene solution was concentrated and dried by distillation. Chromatography of this solution on alumina (Merck), prepared and eluted with 1:1 benzene-hexane, gave 9-phenylanthracene or 9-nitrophenylanthracene followed by a yellow band of 9-phenyl-10-nitrophenylanthracene or 9-nitrophenyl-10-nitrophenylanthracene. Recrystallization from benzene-hexane and/or benzene-ethanol afforded analytical samples. However, 9-*o*-nitrophenyl-10-*m*-nitrophenylanthracene yields a molecular compound of m.p. 218° dec. when crystallized from

benzene and the higher melting point, 244–246°, refers to material recrystallized from ethanol. The reverse syntheses were accomplished by an essentially identical procedure. Yields, melting points, and elemental analyses are recorded in Table I and ultraviolet data are recorded in Table II.

**9-*p*-Chlorophenyl-10-*p*-nitrophenylanthracene.**—This compound was prepared from 9-*p*-nitrophenylanthracene and diazotized *p*-chloroaniline and from 9-*p*-chlorophenylanthracene and diazotized *p*-nitroaniline in the manner described previously for 9-nitrophenyl-10-nitrophenylanthracenes. Both syntheses furnished solid products directly from the respective reaction mixtures. Recrystallization from benzene-ethanol afforded an analytical sample. Pertinent data are listed in Tables I and II.

9-*p*-Chlorophenyl-10-*p*-nitrophenylanthracene may also be prepared directly from anthracene without isolation of the 9-arylanthracene. For example, anthracene was treated with *p*-nitrobenzenediazonium chloride by the procedure previously described<sup>1</sup> and the 9,10-di-*p*-nitrophenylanthracene that precipitated from the reaction mixture was removed by filtration. The filtrate was then treated with diazotized *p*-chloroaniline and the resulting yellow precipitate was isolated by filtration. The yield based on anthracene with 5 equiv. of each diazonium salt amounted to 6%.<sup>8</sup>

**Infrared Spectra.**—The infrared spectra of these compounds are complex. For example, 9-*p*-methoxyphenyl-10-*o*-nitrophenylanthracene exhibits more than twenty strong absorption bands between 6 and 15  $\mu$ . However, all nineteen of these derivatives of 9,10-diphenylanthracene (1–19) exhibit absorption bands, characteristic of the nitro group, at 6.5–6.7 and at 7.4–7.5  $\mu$ . In compounds 10–18, aryl methyl ether absorption bands appear at 8.0–8.2 and at 9.5–9.7  $\mu$ .

**Acknowledgment.**—The authors are indebted to the Aeronautical Research Laboratory, Wright-Patterson Air Force Base, for financial support and to Mr. Derek De Souza for measuring the ultraviolet spectra.

(8) This experiment was performed by Dr. Leon B. Levy.

## The Reaction of Substituted Ureas with Lithium Aluminum Hydride. I. A New Synthesis of Three-Substituted Formamides

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As far as we know, the only previous attempt to reduce ureas with lithium aluminum hydride (LAH) was carried out by Ried and Muller,<sup>1</sup> who, after heating an ether solution of LAH with *sym*-diphenylurea for 30 hr., did not obtain any reaction products.

We have now found that LAH does react with other ureas. In fact, after heating 1,1-diethyl-3-phenylurea with equimolar quantities of LAH in benzene-ether solutions for 14 hr., two fractions could be isolated, besides unreacted urea. The first one was easily recognized as *N*-methylaniline, the other one was identified as *N*-phenyl-*N*',*N*'-diethylformamidine (I), on the basis of microanalysis and of ultraviolet and infrared spectra. The ultraviolet spectrum,<sup>2</sup> with one maximum at 265 m $\mu$  (log  $\epsilon$  4.12), suggested the formation of a double bond conjugated to the benzene ring, as a consequence of the action of LAH on the urea. The in-

(6) O. Diels and F. Bunzl, *Ber.*, **38**, 1486 (1905).

(7) The synthesis of 9-*p*-methoxyphenylanthracene has been reported in ref. 1.

(1) W. Ried and F. Muller, *Chem. Ber.*, **85**, 470 (1952).

(2) This was determined with a Beckman (Model DK) recording instrument in 95% ethanol.