

then attached to the vacuum line and degassed three times in the usual fashion. After being sealed off under vacuum the tube was heated for the desired length of time at 50°. It was then removed from the bath, opened, and the polymer precipitated by addition of the contents of the tube to over 10 times its volume of stirred hexane. The polymer was dissolved in benzene and reprecipitated twice more. The conversion was below 10% in every case. The olefin content of the copolymers was estimated from C,H analyses of samples which had been dried at 60° *in vacuo* for 48 hr. As a check on the accuracy of the method a sample of pure polymethyl methacrylate was also analyzed. The analytical results<sup>21</sup> are: pure poly-MMA, C, 59.92; H, 8.08. (Calcd. C, 59.98; H, 8.05.) MMA-DPE copolymer 1, monomer feed, (MMA)/(DPE) = 97; polymer analysis, C, 60.17; H, 7.95; polymer composition, (MMA)/(DPE) = 235. MMA-DPE copolymer 2, monomer feed, (MMA)/(DPE) = 36; polymer analysis, C, 60.51; H, 7.86; polymer composition, (MMA)/(DPE) = 98. MMA-I copolymer 1, monomer feed, (MMA)/(I) = 40; polymer analysis, C, 60.43; H, 8.06; polymer composition, (MMA)/(I) = 131. MMA-I copolymer 2, monomer feed, (MMA)/(I) = 20; polymer analysis, C, 60.89; H, 8.35; polymer composition, (MMA)/(I) = 72. MMA-II copolymer, monomer feed, (MMA)/(II) = 21; polymer analysis, C, 60.24; H, 7.80; polymer composition, (MMA)/(II) = 208.

Since the polymerizations are all strongly retarded the use

(21) Analyses by Galbraith Labs., Knoxville, Tenn. All analyses are average of duplicate determinations; DPE = diphenylethylene; MMA = methyl methacrylate.

of the usual copolymerization equation to calculate  $r_1$  from these data would not be justified. However, in view of the high (MMA)/(olefin) ratios of all experiments, the only reactions of importance in determining the "copolymer" composition should be reaction 1 and the normal propagation reaction, the amount of methacrylate consumed by reaction 2 being negligible compared to that consumed in the normal propagation reaction. As a result  $r_1$  was calculated from the equation

$$\frac{d(\text{MMA})}{d(\text{olefin})} = \frac{k_p(\text{MMA})}{k_1(\text{olefin})} = r_1 \frac{(\text{MMA})}{(\text{olefin})}$$

The values so obtained were: MMA-DPE,  $r_1 = 2.4, 2.7$ ; MMA-I,  $r_1 = 3.3, 3.6$ ; MMA-II,  $r_1 = 9.9$ .

**Isomerization of Copolymers.**—A weighed amount (about 0.15 g.) of the copolymer was dissolved in about 15 ml. of dry benzene, and the solution was added to a solution of sodium methoxide in methanol prepared by dissolving 0.1 g. of sodium in 10 ml. of anhydrous methanol. The solution was heated to reflux under nitrogen for 5 hr., cooled, poured into a large quantity of water, and the benzene layer washed several times with water. The benzene layer was then dried over sodium sulfate, filtered, and the polymer precipitated by the slow addition of the benzene solution to a large volume of well stirred hexane. The precipitated polymer was dissolved in benzene and reprecipitated with hexane. After thorough vacuum drying its ultraviolet absorption spectrum was determined in chloroform solution.

COLUMBIA, S. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

## Photochemical Reactions in Sunlight. Experiments with Benzo(h)quinoline-5,6-quinone, Monoimine and Monoxime Derivatives in Sunlight and in Dark

BY AHMED MUSTAFA, ABDEL KADER MANSOUR AND AHMED FATHY ABDEL MAWGOOD SHALABY

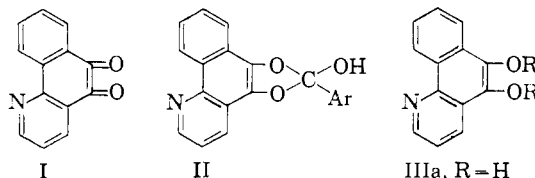
RECEIVED SEPTEMBER 22, 1958

The photochemical addition reaction of aldehydes to heterocyclic nitrogen *o*-quinones, such as benzo(h)quinoline-5,6-quinone (I) has been carried out, yielding the photoproducts listed in Table I. A similar photo-reaction takes place between benzo(h)quinoline-5,6-quinone monoimine and aromatic aldehydes, yielding colorless products believed to have structure such as V, (*cf.* Table II). 2-*p*-Methoxyphenylbenzo(h)quinoline-oxazole (VII, R = C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-*p*) has been obtained either by heating the photo-product of the reaction of benzo(h)quinoline-5,6-quinone monoxime and the aldehyde or by allowing IV to react with *p*-methoxybenzaldehyde in the dark, in the presence of piperidine. The photochemical addition of I to olefins such as stilbene,  $\alpha,\alpha$ -diphenylethylene, triphenylethylene and benzaldehyde, has been investigated. The photoproducts are listed in Table III. 3-Phenylbenzo(f)quinoxaline-5,6-quinone (XV) and compound I react with ethereal diazomethane solution and with diphenyldiazomethane to give the corresponding methylene ethers (XVIIa, XVIIb and XVIIc, XVIIb). Whereas, I is stable toward the action of 9-diazofluorene, XV reacts under the given experimental conditions to yield XVIIc. Benzo(h)quinolinooxazole (VII, R = H) is obtained either by the action of ethereal diazomethane on IV and/or VIII or by the action of dimethyl sulfate on VIII.

In continuation of our previous work, the action of aromatic aldehydes on heterocyclic nitrogen *o*-quinones has been extended.<sup>1-3</sup>

We have allowed the yellow benzo(h)quinoline-5,6-quinone (I) to react with aromatic aldehydes in the absence of oxygen and have found that addition takes place in molecular proportions. The colorless photo-products (*cf.* Table I) are obtained in good yield in most cases and separate during exposure. It is believed that these 2-arylbenzo(h)-

quinoline-(5,6)-1:3-dioxol-2-ol derivatives have constitutions such as II or the corresponding open form.



(1) A. Mustafa, A. H. E. Harhash, A. K. E. Mansour and S. M. A. E. Omran, *THIS JOURNAL*, **78**, 4306 (1956).

(2) A. Schönberg, A. Mustafa and S. M. A. D. Zayed, *ibid.*, **75**, 4302 (1953).

(3) It has been shown that the photo-addition of aldehydes to *o*-quinones is a general reaction which may be carried out with *o*-benzoquinone derivatives (A. Schönberg, *et al.*, *J. Chem. Soc.*, 1364 (1951)),  $\alpha$ -naphthoquinone derivatives (A. Schönberg, *ibid.*; A. Mustafa, *et al.*, ref. 1. phenanthraquinone (A. Mustafa, *ibid.*, 997 (1947); A. Mustafa, *Nature*, **166**, 108 (1950)), acenaphthenequinone (A. Sircar and S. Sen, *J. Indian Chem. Soc.*, 997 (1947)), and chrysenequinone (A. Mustafa, *J. Chem. Soc.*, 1034 (1951)).

Compound II (Ar = C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-*p*) is typical of compounds having such structures. It is colorless, insoluble in cold aqueous sodium hydroxide solution and gives no color with ferric chloride. It yields *p*-methoxybenzoic acid and I on treatment with cold concentrated sulfuric acid. The formation of I may be attributed to the action of sulfuric acid on the intermediate 5,6-dihydroxybenzo-

TABLE I  
PHOTO-ADDITION PRODUCTS FROM BENZO(h)QUINOLINE-5,6-QUINONE (I)

Addition products II (yield, %) Ar =	o-Quinone I wt., g.	Aldehyde and (wt., g.)	Benzene, ml.	Time of irradiation, days	M.p., °C. <sup>c</sup>	Solvent for crystn. <sup>e</sup>	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
C <sub>6</sub> H <sub>5</sub> (84)	0.9	Benzaldehyde (0.65)	35	10 <sup>a</sup>	207	A	C <sub>20</sub> H <sub>13</sub> NO <sub>3</sub>	76.19	75.54	4.12	4.44	4.44	4.24
C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (89)	.8	<i>p</i> -Methoxybenzaldehyde (0.62)	30	8 <sup>a</sup>	212	B	C <sub>21</sub> H <sub>15</sub> NO <sub>4</sub>	73.04	73.18	4.34	3.73	4.05	3.92
C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (80)	.6	<i>p</i> -Tolualdehyde (0.5)	25	15 <sup>b</sup>	205	B	C <sub>21</sub> H <sub>15</sub> NO <sub>3</sub>	76.59	76.49	4.55	4.91	4.25	3.83
C <sub>6</sub> H <sub>4</sub> Cl- <i>o</i> (61)	.8	<i>o</i> -Chlorobenzaldehyde (0.7)	30	12 <sup>b</sup>	190	B	C <sub>20</sub> H <sub>12</sub> ClNO <sub>3</sub> <sup>d</sup>	68.66	68.45	3.43	3.41	4.00	4.00

<sup>a</sup> March. <sup>b</sup> April. <sup>c</sup> Melting points are uncorrected. <sup>d</sup> Calcd: Cl, 10.15. Found: Cl, 10.3. <sup>e</sup> A, alcohol; B, benzene.

TABLE II  
PHOTO-ADDITION PRODUCTS FROM BENZO(h)QUINOLINE-5,6-QUINONEMONOIMINE (IV)

V; Ar =	IV; wt., g.												
C <sub>6</sub> H <sub>5</sub> (88)	0.8	Benzaldehyde (0.7)	20	8 <sup>a</sup>	227		C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	76.43	76.32	4.45	4.69	8.91	9.06
C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (87)	.8	<i>o</i> -Methoxybenzaldehyde (0.8)	30	20 <sup>b</sup>	197		C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	73.25	73.29	4.65	4.67	8.13	8.15
C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>o</i> (89)	.9	<i>p</i> -Methoxybenzaldehyde (0.7)	25	8 <sup>a</sup>	218		C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	73.25	72.98	4.65	4.45	8.13	7.98
C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (76)	.8	<i>p</i> -Tolualdehyde (0.7)	30	8 <sup>a</sup>	205		C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	76.82	76.33	4.87	5.04	8.53	8.72
C <sub>6</sub> H <sub>4</sub> Cl- <i>o</i> (60)	.8	<i>o</i> -Chlorobenzaldehyde (0.6)	30	10 <sup>a</sup>	235		C <sub>20</sub> H <sub>13</sub> ClN <sub>2</sub> O <sub>2</sub> <sup>c</sup>	68.86	68.74	3.73	3.70	8.03	7.81

<sup>a</sup> August. <sup>b</sup> September. <sup>c</sup> Calcd.: Cl, 10.18. Found: Cl, 10.47.

TABLE III  
PHOTO-ADDITION PRODUCTS FROM BENZO(h)QUINOLINE-5,6-QUINONE (I)

	I; wt., g.	Ethylene											
XIa (75)	1.0	Stilbene (0.85)	30	12 <sup>a</sup>	250	A <sup>c</sup>	C <sub>27</sub> H <sub>19</sub> NO <sub>2</sub>	83.29	83.31	4.88	5.04	3.59	3.50
XIb (62)	0.8	$\alpha,\alpha$ -Diphenylethylene (0.6)	25	15 <sup>a</sup>	198	B	C <sub>27</sub> H <sub>19</sub> NO <sub>2</sub>	83.29	83.21	4.88	4.91	3.59	3.24
XIc (58)	.8	Triphenylethylene (0.65)	25	15 <sup>b</sup>	257	A	C <sub>33</sub> H <sub>23</sub> NO <sub>2</sub>	85.16	85.16	4.94	5.19	3.01	2.84
XII (69)	.8	Benzaldehyde (0.6)	30	15 <sup>a</sup>	302	A	C <sub>23</sub> H <sub>17</sub> NO <sub>4</sub>	77.95	77.70	3.94	3.80	3.24	3.30

<sup>a</sup> July. <sup>b</sup> August. <sup>c</sup> A, benzene; B, alcohol.

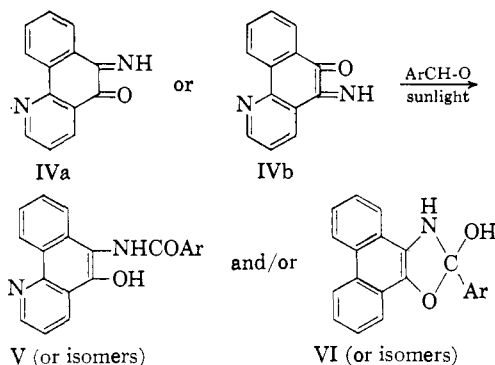
TABLE IV  
ACTION OF AROMATIC ALDEHYDES ON IV, VIII AND IX IN THE DARK

Compound	Aldehyde	Adduct, R =	Color with H <sub>2</sub> SO <sub>4</sub>	M.p., °C.	Yield, %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
IV	Benzaldehyde	VII, C <sub>6</sub> H <sub>5</sub>	Yellow	184	92	C <sub>26</sub> H <sub>19</sub> ON <sub>2</sub>	81.08	80.98	4.06	4.13	9.56	9.63
IV	<i>p</i> -Methoxybenzaldehyde	VII, C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i>	Brown	194	90	C <sub>27</sub> H <sub>19</sub> O <sub>2</sub> N <sub>2</sub>	77.30	76.89	4.29	4.18	8.58	8.54
IV	<i>o</i> -Methoxybenzaldehyde	VII, C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>o</i>	Violet	128	50	C <sub>21</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub>	77.30	76.95	4.29	4.21	8.58	8.37
IV	<i>o</i> -Ethoxybenzaldehyde	VII, C <sub>6</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub> - <i>o</i>	Violet	148	70	C <sub>22</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub>	77.64	77.74	4.70	4.98	8.23	8.20
IV	<i>p</i> -Tolualdehyde	VII, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	Yell. green	191	85	C <sub>21</sub> H <sub>14</sub> ON <sub>2</sub>	81.29	81.14	4.51	4.57	9.03	8.85
VIII	Benzaldehyde	VII, C <sub>6</sub> H <sub>5</sub>										
VIII	<i>o</i> -Methoxybenzaldehyde	VII, C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i>										
IX	Benzaldehyde	Xb <sup>a</sup>										

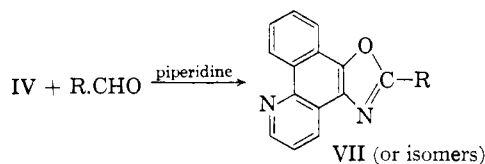
<sup>a</sup> Compound Xb was identified by m.p. and mixed m.p. with an authentic sample (cf. A. Schönberg, N. Latif, R. Moubasher and W. I. Awad, *J. Chem. Soc.*, 374 (1950)).

(h)quinoline (IIIa). Compound IIIa has been prepared by reduction of I with phenylhydrazine<sup>4</sup>; it is readily converted to 5,6-diacetoxy-benzo(h)-quinoline (IIIb) by the action of acetic anhydride.

**Benzo(h)quinoline-5,6-quinone Monoimine and Aromatic Aldehydes.**—Benzo(h)quinoline-5,6-quinone monoimine (IVa or IVb) does not react with benzaldehyde in benzene solution at room temperature in the dark, but that a reaction occurs in sunlight with the formation of colorless photo-products which separate during exposure and are believed to have structures such as V or its isomers.<sup>5</sup> Similar reactions were carried out with *p*-methoxy, *o*-methoxy, *o*-chlorobenzaldehyde, *m*-tolualdehyde and *p*-tolualdehyde. The photo-products are colorless and are partially soluble in aqueous sodium hydroxide solution, completely soluble in alcoholic sodium hydroxide solution with yellow color and give a green color with alcoholic ferric chloride.<sup>6,7</sup>



When IV was allowed to react with benzaldehyde in the dark, in the presence of piperidine, the corresponding oxazole derivative (VII or isomer) was obtained in good yield.

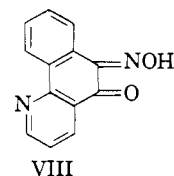


A similar reaction was observed with *p*-methoxy, *o*-methoxy, *o*-ethoxybenzaldehyde and *p*-tolualdehyde. This reaction is similar to that described by Stein and Day<sup>8</sup> for the preparation of phenanthroxazoles. The reactions described may support the suggestion of the latter authors that IV acts as an active hydrogen compound and adds to the aldehyde under the catalytic influence of piperidine.

**Benzo(h)quinoline-5,6-quinone Monoxime and Aromatic Aldehydes.**—While the mechanism of the action of aromatic aldehydes on *o*-quinone monoximes is not known, the over-all results may be summarized: the oxime (VIII or isomer) and *p*-methoxybenzaldehyde do not react in benzene in

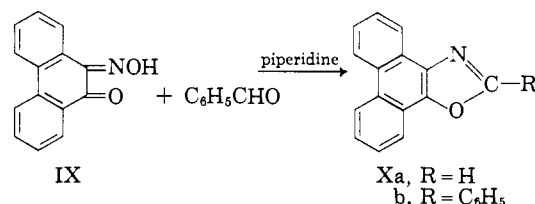
- (4) G. Badger, R. S. Pearce and R. Pettit, *J. Chem. Soc.*, 3204 (1951).  
 (5) A. Mustafa and M. Kamel, *THIS JOURNAL*, **77**, 5030 (1955).  
 (6) A. Schönberg, *et al.*, *J. Chem. Soc.*, 1364 (1951).  
 (7) R. F. Moore and W. A. Waters, *ibid.*, 238 (1953); H. Klinger, *Ann.*, **249**, 137 (1888).  
 (8) C. W. C. Stein and A. R. Day, *THIS JOURNAL*, **64**, 2567 (1942).

the dark at room temperature; in sunlight, however, a product was formed which on heating yields 2-*p*-methoxyphenylbenzo(h)quinoline-oxazole (VII, R = C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-*p*).<sup>9</sup>

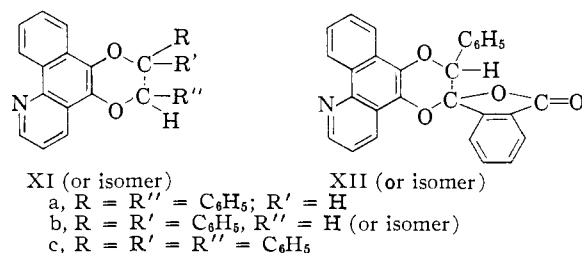


We have also found that VIII reacts with aromatic aldehydes, *e.g.*, benzaldehyde and *p*-methoxybenzaldehyde to yield VII (R = C<sub>6</sub>H<sub>5</sub>) and VII R = C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-*p*), respectively, when the corresponding reactants are heated without a solvent in the presence of piperidine.

A similar reaction, has now been observed when phenanthraquinone monoxime (IX) is heated with benzaldehyde without a solvent in the presence of piperidine, yielding 2-phenylphenanthroxazole (Xb). No reaction takes place in the absence of the catalyst.



**Benzo(h)quinoline-5,6-quinone and Ethylene.**—We have continued investigations on the action of ethylenes on *o*-quinones in sunlight,<sup>10,11</sup> and have studied the action of stilbene,  $\alpha,\alpha$ -diphenylethylene, triphenylethylene and benzaldehyde on I and have found that, whereas no reaction takes place in the dark, in sunlight colorless products (XIa-c and XII) are formed. Compound XIa regenerated the starting materials on heating.



**Reactions with Diazoalkanes.**—Recently, it has been shown that 1,2-benzophenazine-3,4-quinone (XIII) reacts with diazomethane<sup>2</sup> and with

(9) This reaction is similar to the formation of 2-phenylphenanthroxazole (Xb) by the action of heat on the product obtained by exposing a mixture of phenanthraquinone monoxime (IX) and benzaldehyde to sunlight; *cf.* A. Schönberg, *et al.*, *J. Chem. Soc.*, 374 (1950).

(10) A. Schönberg, A. Mustafa and co-workers, *ibid.*, 387 (1944); 551 (1945); 2126 (1948); *Chem. Revs.*, **40**, 190 (1948); A. Mustafa and A. M. Islam, *J. Chem. Soc.*, S 81 (1949); A. Mustafa, *ibid.*, S 83 (1949); 1034 (1951).

(11) For the mechanism of such photo-additions (*cf.* G. O. Schenk, *Naturwissenschaften*, **40**, 229 (1953); G. O. Schenk and G. A. Schmidt Thome, *Ann.*, **584**, 199 (1953) and A. Schönberg, *et al.*, *THIS JOURNAL*, **77**, 3850 (1955)); *cf.* also "Preparative Organische Photochemie," A. Schönberg, Springer-Verlag, Berlin, Göttingen, Heil Heidelberg, 1958, p. 93.



benzene, but is difficultly soluble in petroleum ether. It gives a yellow color with sulfuric acid and is insoluble in aqueous sodium hydroxide solution.

*Anal.* Calcd. for  $C_{13}H_5N_2O$ : C, 75.00; H, 3.84; N, 13.46. Found: C, 74.59; H, 3.65; N, 13.12.

The corresponding phenazine derivative was obtained by refluxing a solution of 0.6 g. of I and 0.6 g. of *o*-phenylenediamine in 50 ml. of glacial acetic acid for half an hour. The product was recrystallized from glacial acetic acid in pale yellow crystals, m.p. 221°, yield ca. 91%. It gives a red color with sulfuric acid and is sparingly soluble in common organic solvents.

*Anal.* Calcd. for  $C_{13}H_{11}N_3$ : C, 81.13; H, 3.91; N, 14.94. Found: C, 81.19; H, 3.80; N, 14.63.

**5,6-Diacetoxybenzo(h)quinoline (IIIb).**—5,6-Dihydroxybenzo(h)quinoline (IIIa) was obtained after the procedure described by Badger, Pearce and Pettit<sup>4</sup> by the action of phenylhydrazine on 1 g. of I; IIIa formed colorless crystals from ethyl alcohol, m.p. 207°, yield ca. 57%. It gave no color with aqueous ferric chloride solution and was soluble in aqueous sodium hydroxide solution with green color.

*Anal.* Calcd. for  $C_{13}H_9NO_2$ : C, 73.93; H, 4.26; N, 6.63. Found: C, 73.71; H, 3.61; N, 6.53.

A solution of 0.8 g. of IIIa in 15 ml. of acetic anhydride<sup>4</sup> was refluxed for half an hour. The cooled reaction mixture gave colorless crystals (0.65 g.) which were recrystallized from acetic anhydride, m.p. 194°; IIIb is insoluble in cold aqueous sodium hydroxide solution and gives no color with ferric chloride.

*Anal.* Calcd. for  $C_{17}H_{13}NO_4$ : C, 69.15; H, 4.40; N, 4.74. Found: C, 68.75; H, 4.21; N, 4.29.

**Photochemical Reactions with I and IV in Sunlight. General Remarks.**—The photochemical reactions were carried out as described in the previous publications.<sup>1</sup>

**Photochemical Reaction of VIII with *p*-Methoxybenzaldehyde.**—One gram of VIII and 0.8 g. of *p*-methoxybenzaldehyde in 45 ml. of benzene were exposed to sunlight for 27

days (October). The deposit that separated during exposure was crystallized from ethanol into colorless crystals, m.p. 225°, yield ca. 89%. The photo-product gave a yellow color with concentrated sulfuric acid, and developed a green color with ferric chloride. It was partially soluble in cold aqueous sodium hydroxide solution with a yellow color.

When the photo-product (0.8 g.) was heated at 260° (bath-temp.), under reduced pressure (oil-pump) for 15 minutes, a sublimate was obtained which upon crystallization from ethanol proved to be (VII, R =  $C_6H_4OCH_3$ -*p*) (m.p. and mixed m.p.).

**Action of Sulfuric Acid on II (Ar =  $C_6H_4OCH_3$ -*p*).**—Compound II (Ar =  $C_6H_4OCH_3$ -*p*) (0.8 g.) was dissolved in 5 ml. of concentrated sulfuric acid, and the reaction mixture was allowed to stand at room temperature overnight. It was then poured into cold water and neutralized with sodium carbonate. The yellow substance that separated was crystallized from benzene and identified as I (m.p. and mixed m.p. and the formation of the corresponding phenazine derivative). Acidification of the alkaline solution, gave *p*-methoxybenzoic acid.

**Thermal Decomposition of XIa.**—One gram of XIa was heated at 265–270° (bath-temp.) for 1.5 hours under reduced pressure. The colorless sublimate on the cooled parts of the reaction vessel was collected and crystallized from ethanol (ca. 0.23 g.) and was identified as stilbene (m.p. and mixed m.p.). The contents of the reaction vessel were recrystallized from benzene (0.34 g.) and identified as I (m.p. and mixed m.p.).

**Action of Aromatic Aldehydes on IV in the Dark. General Procedure.**—A mixture of 0.01 mole of IV, 0.03 mole of the appropriate aldehyde and few drops of piperidine in 50 ml. of absolute ethanol was refluxed (steam-bath) for two hours. The product which separated on cooling was recrystallized from ethanol into colorless crystals (VII) (*cf.* Table IV). The resulting oxazoles are insoluble in aqueous sodium hydroxide solution and their alcoholic solutions give no color when treated with ferric chloride.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

## Substituent Effects on Naphthalene. II. Association Constants of Substituted Naphthalene—Picric Acid Complexes Determined Spectrophotometrically

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RECEIVED DECEMBER 5, 1958

Association constants of twenty-two substituted naphthalenes have been measured using a spectrophotometric method. The values obtained are compared with values previously obtained using the partition method. A dependence of the value of the association constant on the wave length of measurement is noted and interpreted on the basis of "contact" charge-transfer or "solvent perturbation."

The formation of molecular complexes between polynitroaromatic hydrocarbons and aromatic compounds has been investigated quantitatively by the partition method<sup>2</sup> and by an adaptation of the spectrophotometric method described by Benesi and Hildebrand.<sup>3</sup> It has been frequently noted that the partition method, in which the partition coefficient of the polynitro compound between water and a non-polar solvent is measured with and without the donor in the non-polar phase, gives a higher value for the association constant than does the spectrophotometric method. Ross and Kuntz<sup>4</sup> have suggested that the partition method measures a number of interactions such as dipole-dipole interactions and intermolecular hydrogen

bonding while the spectrophotometric method measures only complexation due to charge-transfer bonding. In the theory of molecular-compound formation proposed by Mulliken,<sup>5</sup> the charge-transfer state, in which the aromatic donor compound has donated an electron to the polynitro acceptor compound, is responsible for the characteristic absorption of the complex.

A recent measurement of the association constant of naphthalene picrate in chloroform solution by Foster<sup>6</sup> has resulted in a value of  $K = 2.4$  which is very near the value found using the partition method.<sup>7</sup> The difference from the value previously reported by Ross and Kuntz<sup>4</sup>,  $K = 0.99$ , was attributed to the large excess of donor compound. To minimize any effect due to excess

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