reaction starts from this state (because of the shape of the potential surface) before radiationless conversion to the first excited state has occurred. If this is the case, then any discussion in terms of the properties of the first excited state will be inadequate. But before a sound discussion of these reactions is possible, extensive studies of photochemical transformations using monochromatic light are essential.

Photolytic Rearrangement and Halogen-Dependent Photocylization of Halophenylnaphthalenes. II[1]

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Abstract: Photolysis of 1-(*o*-chlorophenyl)naphthalene proceeds with unusual efficiency to give a high yield of fluoranthene under a wide variety of conditions, while 1-(*o*-iodophenyl)naphthalene gives a variety of rearrangement and solvolytic products but virtually no fluoranthene. The bromo derivative exhibits intermediate behavior. The above chloro compound produces fluoranthene in somewhat better yield and quantum yield in more polar solvents. Treatment of the iodo compound with thermally generated phenyl radicals produces substantial quantities of fluoranthene. 1-(*o*-Iodophenyl)naphthalene and 1-iodo-8-phenylnaphthalene are photochemically interconvertible and their chloro and bromo analogs behave similarly. 1-*o*-Chlorophenyl-5-methoxynaphthalene produces only a slightly higher ratio of fluoranthene derivative to other products than does 1-(*o*-chlorophenyl)-naphthalene. The results are all consistent with a mechanism where the initial photochemical step is a homolytic cleavage to give an aromatic radical and a halogen atom. The radical may undergo several reactions, but the product distribution is controlled by the reactivity of the halogen coradical.

In contrast to the large number of photocyclization reactions of aromatic compounds which have been found to produce a six-membered ring, reports of five-membered rings formed under these conditions are rare. Linschitz and Grellmann and Bowen and Eland[2] noted the photocyclodehydrogenation of diphenylamines which produced carbazoles. The former group found spectroscopic evidence for a dihydrocarbazole intermediate. Grellmann and Tauer[3] more recently reported several other photolytic heterocyclic ring closures where the newly formed five-membered ring contained six π electrons. Kampmeier and Evans[4] reported a photolytic cyclization reaction of 2-iodo-2′-thiomethoxybiphenyl which resulted in dibenzothiophene formation. Their evidence indicated that the ring-closure step was a nonphotochemical reaction of the photochemically produced radical species.

Reports of photochemical generation of five-membered rings containing five π electrons are even less common. An early study[5] indicated that irradiation of the trityl radical produces 9,9′-diphenyl-9,9′-difluorenyl and triphenylmethane. Badoche[6] found that 9-iodo-10,11,12-triphenyltetracene gave 9,10-*o*-phenylene-11,12-diphenyltetracene, when irradiated. The mechanistic details of these reactions have gone unexplored.

In contrast to the photocyclization of aromatics, five-membered ring formation frequently occurs on irradiation of dienes.[7]

We have examined the photochemical behavior of the 1-(*o*-halophenyl)naphthalenes and related compounds as part of an effort to understand the requirements for photolytic generation of five-membered rings in aromatic systems. Our interest in a detailed study was aroused by the initial observation[1] that 1-(*o*-chlorophenyl)naphthalene photocyclized to fluoranthene in high yield, while 1-(*o*-iodophenyl)naphthalene did not.

Results

Synthesis and Spectroscopy. 1-(*o*-Chlorophenyl)-naphthalene (**1**, X = Cl), 1-(*o*-chlorophenyl)-5-methoxynaphthalene (**6**), and 1-(*p*-chlorophenyl)naphthalene were prepared by the method of Johnson and Waters.[8] The bromo and iodo compounds **1** (X = Br and I) were synthesized as described in the Experimental Section. 9-(*o*-Chlorophenyl)anthracene[9] was made by heating a mixture of anthracene, *o*-chloroaniline, and amyl nitrite in benzene.

The compound 1-iodo-8-phenylnaphthalene (**7**) was prepared in several steps from the known 1-bromo-8-nitronaphthalene.[10] Attempts to prepare the analogous chloro and bromo compounds *via* the same route failed.

The ultraviolet absorption spectra were obtained in methanol. The band maxima and their extinction coefficients are reported in Table I. The compounds

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[1] A preliminary communication describing a portion of this work has appeared: W. A. Henderson, Jr., and A. Zweig, *J. Amer. Chem. Soc.*, **89**, 6778 (1967).

[2] H. Linschitz and K. H. Grellmann, *ibid.*, **85**, 1881 (1963); **86**, 303 (1964); E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc.*, 202 (1963).

[3] K. H. Grellmann and E. Tauer, *Tetrahedron Lett.*, 1909 (1967).

[4] J. A. Kampmeier and T. R. Evans, *J. Amer. Chem. Soc.*, **88**, 4096 (1966).

[5] J. Schmidlin and A. Garcia-Banus, *Ber. Deut. Chem. Ges.*, **45**, 1344 (1912).

[6] M. Badoche, *Bull. Soc. Chim. Fr.*, **9**, 393 (1942).

[7] R. Srinivasan, Abstracts of Papers, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1–5, 1968, P-89.

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

[9] F. A. Vingiello, M. O. L. Spangler, and J. E. Bondurant, *J. Org. Chem.*, **25**, 2091 (1960).

[10] H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 571 (1937).

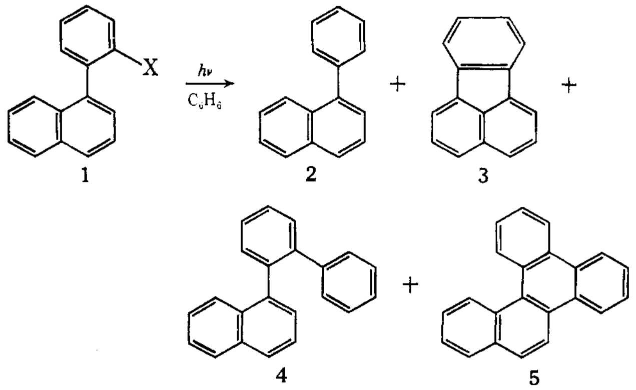
Table I. Spectral Properties of Halophenylnaphthalenes

Compound	Absorption maxima[a] $\lambda_{m\mu}$ (log ϵ)	Fluoresc.[b] λ_{max}, mμ	Phosphores.[b] λ_{max}, mμ	τ_P, sec	ϕ_P/ϕ_F
1-(*o*-Chlorophenyl)naphthalene	262 sh (3.65), 272 (3.84), 281 (3.93), 287 sh (3.85), 291 (3.83), 313 (2.81)	320 sh, 326, 342,[d] 354	473,[c] 480,[d] 491, 518,[c] 558	1.7	3.7
1-(*o*-Bromophenyl)naphthalene	262 sh (3.68), 272 (3.86), 281 (3.94), 287 sh (3.85), 291 (3.84), 313 (2.87)	~345	472,[c] 477,[d] 516,[e] 555	0.5	>30
1-(*o*-Iodophenyl)naphthalene	262 sh (3.68), 272 (3.85), 282 (3.93), 288 (3.83), 292 (3.82), 314 (2.82)		473,[c] 477,[d] 489, 516,[e] 554	0.05	>300
1-Iodo-8-phenylnaphthalene	289 sh (3.90), 299 (3.97), 307 sh (3.96), 313 sh (3.86)		490,[c] 520, 556, 600	0.001	>300
1-(*o*-Chlorophenyl)-5-methoxynaphthalene	290 sh (3.89), 298 (3.94), 308 sh (3.86), 314 sh (3.79) 323 (3.66)		475,[c] 486, 493 sh, 523, 564	1.7	0.81
1-(*p*-Chlorophenyl)naphthalene	263 sh (3.84), 275 sh (3.99), 281 (4.00)	322 sh, 328, 343,[e] 358	487,[c] 511, 541,[e] 585	0.78	

[a] In methanol. [b] In 3-methylpentane glass, 10^{-3} *N*, 77°K, 313-mμ excitation. [c] Onset (10% λ_{max}). [d] 0–0 band max. [e] Strongest band.

studied were all phosphorescent at 77°K in a 3-methylpentane glass. The chlorine- and bromine-substituted compounds also exhibited a weak fluorescence emission. The phosphorescence emission maxima, the phosphorescence lifetimes, and the integrated intensities of phosphorescence to fluorescence (ϕ_P/ϕ_F) under the conditions employed are also reported in Table I.

Irradiation in Benzene. On irradiation with 313-mμ light in benzene, the bromo compound **1** (X = Br) gave yellow-orange solutions from which four products were isolated. These were shown to be 1-phenylnaphthalene (**2**), fluoranthene (**3**), 1-(2-biphenylyl)-naphthalene (**4**), and benzo[*g*]chrysene (**5**). All four products were isolated by chromatography on alumina. 1-Phenylnaphthalene was identified by identity of its infrared and ultraviolet spectra and retention times on vpc with those of authentic material. Products **3**, **4**, and **5** were identified by melting point and mixture melting point with authentic material[11] and by their infrared and ultraviolet spectra.



Surprisingly, irradiation of the chloro or iodo compounds **1** (X = Cl or I) gave pale yellow or deep violet solutions with markedly different product ratios as determined by vpc. At least one run of each type was checked by chromatography of the reaction mixture on alumina and spectroscopic analysis of the products. In all important cases, products were isolated and identified by melting point, mixture melting point, etc. Product recoveries were all >90%. Analyses of reaction mixtures from irradiation of ~3 × 10^{-3} *N* solutions of the 1-(*o*-halophenyl)naphthalenes **1** at 254 and 300 mμ in benzene deoxygenated by bubbling with nitrogen are given in Table II. The results from untreated benzene solutions were very similar but not identical.

Table II. Products Formed on Irradiation of 1-(*o*-Halophenyl)naphthalenes **1** in Benzene[a]

Wavelength, mμ	Halogen	Conversion, %	Products, %[b]: Phenylnaphthalene, **2**	Fluoranthene, **3**	Arylation products, **4 + 5**
300	Cl	13	17	59	24
		5[c]	14	72	14
	Br	30	58	5	37
		72	46	8	46
	I	80	18	0	82
		45[c]	15	1	84
254	Cl	60	10	72	18
	Br	45	75	6	20
	I	51	59	0	41

[a] Approximately 3 × 10^{-3} *N* solutions bubbled with N_2 irradiated 1–8 hr at 25°. [b] Normalized to 100%. [c] In addition to products listed, a vpc peak believed to be that of the 1-halo-8-phenylnaphthalene (<2%) was detected.

All four products were stable in refluxing benzene in the presence or absence of oxygen. The halophenylnaphthalene reactants were also thermally stable at elevated temperature. Heating **1** (X = Cl or X = I) to 300° for 1 hr in sealed tubes gave only starting material and <1% of 1-phenylnaphthalene (**2**). While **2**, **3**, and **5** were stable to ultraviolet light under the experimental conditions,[12] in the presence or absence of oxygen and/or iodine, 1-(2-biphenylyl)naphthalene (**4**) was converted smoothly to benzo[*g*]chrysene (**5**). Since one of the products is thus photoreactive, the ratios of products will vary with the time of irradiation and extent of conversion. This was confirmed for all three 1-(*o*-halophenyl)naphthalenes. The variation of product concentrations with time for a typical run of the bromo compound (**1**, X = Br) is shown in Figure 1.

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[11] The 1-(2-biphenylyl)naphthalene was prepared by the method of P. G. Copeland, R. E. Dean, and D. McNeil, *J. Chem. Soc.*, 1687 (1960); benzo[*g*]chrysene was prepared by photocyclization of **4** (see Experimental Section).

[12] See also W. Carruthers, *J. Chem. Soc.*, *C*, 1525 (1967).

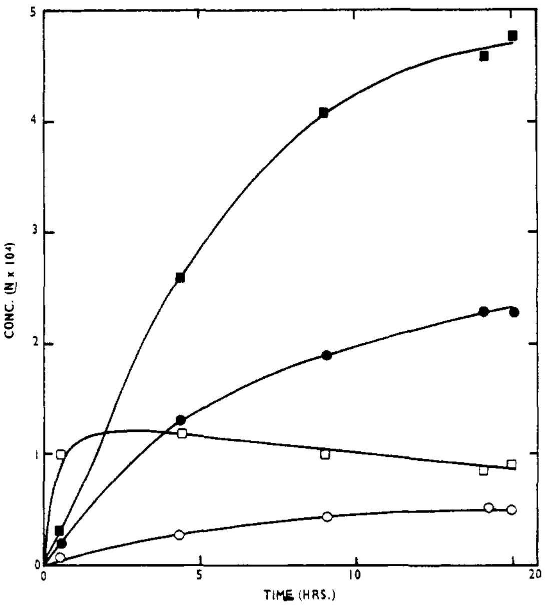

Figure 1. Products formed on irradiation of 1-(*o*-bromophenyl)-naphthalene as a function of time: ●, 1-phenylnaphthalene (**2**); ○, fluoranthene (**3**); □, 1-(2-biphenylyl)naphthalene (**4**); ■, benzo-[*g*]chrysene (**5**).

While a threefold change in intensity of the 313-mμ source gave no statistically significant change in product ratios for **1**, changing the concentration of **1** *did* have a significant effect on the product ratios. An increase in the concentration of **1**, X = Cl, from $\sim 10^{-3}$ to $\sim 10^{-1}$ *N* led, on irradiation with 300-mμ light, to a greatly increased yield of 1-phenylnaphthalene (**2**) and decreased yield of fluoranthene **3** (Table III). A similar change in concentration of **1** (X = Br) or **1** (X = I) led to a large increase in the yield of **2** and a decrease in the yield of **4** plus **5**.

Table III. Effect of Concentration on Product Ratios on Irradiation of 1-(*o*-Halophenyl)naphthalenes **1** in Benzene[a]

			Products, %[b]		
Halogen	Concn, *N*	Conversion, %	Phenylnaphthalene **2**	Fluoranthene **3**	Arylation products **4** + **5**
Cl	9.7×10^{-2}	15	33	50	17
		5	37	34	29
	9.7×10^{-4}	75	5	80	15
		14	10	65	25
Br	7.9×10^{-2}	19	74	7	20
	7.9×10^{-4}	88	21	9	69
I	8.3×10^{-2}	29	57	0	43
	8.3×10^{-4}	94	9	2	89

[a] Solutions in 1-mm uv cells bubbled with nitrogen and irradiated 30–60 min with 300-mμ light. [b] Normalized to 100%.

When **1** (X = Br) is irradiated with 313-mμ light at −80° or even −20° in benzene or in a hydrocarbon solvent, no fluoranthene emission is observed. Moreover, when such solutions are warmed to room temperature, there is still no fluorescence of **3** on excitation with ultraviolet light, and only starting material can be recovered.

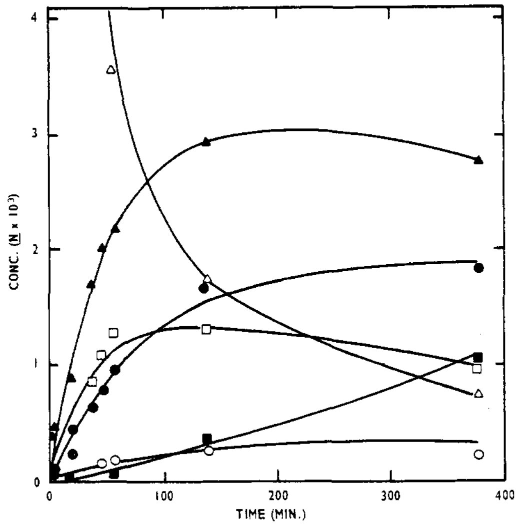

Figure 2. Products formed on irradiation of 1-iodo-8-phenylnaphthalene as a function of time: △, 1-iodo-8-phenylnaphthalene (**7**); ▲, 1-(*o*-iodophenyl)naphthalene (**1**, X = I); ●, 1-phenylnaphthalene (**2**); ○, fluoranthene (**3**); □, 1-(2-biphenylyl)naphthalene (**4**); ■, benzo[*g*]chrysene (**5**).

Photolysis of 1-iodo-8-phenylnaphthalene (**7**) in benzene with 313-mμ light resulted in the simultaneous formation of 1-(*o*-iodophenyl)naphthalene (**1**, X = I) and the other products (**2**–**5**) previously found to be derived from **1**. A plot of the rate of appearance of the products as a function of time is given in Figure 2. A very deliberate search was made of vpc curves for evidence of 1,8-diphenylnaphthalene.[13] Within the limits of detectability of the method (~0.1%), none was found.

Since **7** gives **1** (X = I) on irradiation, a search was made of earlier vpc curves for traces of **7** formed by the reverse reaction, the irradiation of **1** (X = I). In those cases where irradiation of **1** (X = I) was carried to only a small fraction of completion, a small peak (<1%) with the same retention time as **7** was found. The peak for **7** appeared immediately after that for the *o*-iodo compound (**1**, X = I). On further study, vpc curves for reaction mixtures of **1** (X = Cl) and **1** (X = Br) occasionally showed small (<1%) peaks just after those of the starting materials. These are tentatively ascribed to 1-chloro- and 1-bromo-8-phenylnaphthalene, since they appear only during the initial stages of reaction and disappear on longer irradiation. Similarly, 1-(*o*-chlorophenyl)-5-methoxynaphthalene (**6**), on irradiation in benzene with 254-mμ light for short periods of time, gave reaction mixtures in which up to 20% of the photoproduct was a compound with a retention time slightly longer than **6**. The product could not be separated from **6** which was always present in much greater amounts. On longer irradiation, the unknown compound decreased in concentration; hence, it is assumed to be the isomer 1-phenyl-5-methoxy-8-chloronaphthalene (*cf.* Table IV).

Irradiation in Methanol. Irradiation of the 1-(*o*-halophenyl)naphthalenes was also carried out in methanol. With the 254-mμ light source and the solvent bubbled with nitrogen, **1** (X = Cl) gave 35% **2** and 65% **3**, **1** (X = Br) gave 68% **2** and 32% **3**, while **1** (X = I) gave 100% **3**. In addition, a very small amount (~0.5%) of 1-(*o*-methoxyphenyl)naphthalene (**12**) was

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[13] A sample of authentic 1,8-diphenylnaphthalene, kindly supplied by Professor H. O. House, was used for determination of the correct retention time.

Table IV. Products Formed on Irradiation of 1-(*o*-Chlorophenyl)-5-methoxynaphthalene (**6**)[a]

Solvent concn, *N*	λ, mμ	Conversion[c] %	Products, %[b] Phenylnaphthalene **8**	Fluoranthene **9**	Arylation products **10** + **11**
Benzene	300	5	4	78	18
8.7×10^{-3}	254	13	4	76	20
Methanol	300	35	5	95	
5.0×10^{-3}	254	30	8	92	

[a] All solutions bubbled with nitrogen and irradiated 60 min with 300-mμ light. [b] Normalized to 100%. [c] In addition to the products listed, a vpc peak ascribed to 1-phenyl-5-methoxy-8-chloronaphthalene was detected. Its area was 2–20% of the total.

Table V. Quantum Yields of Disappearance, ϕ_D, for Halophenylnaphthalenes[a]

Solvent	Compd	λ, mμ	ϕ_{meas}	ϕ_D[b]
Benzene	**1** (X = Cl)	313	3.7×10^{-4} [c]	9.3×10^{-4}
		254	7.4×10^{-4} [c]	10.0×10^{-4}
	1 (X = Br)	313	11.0×10^{-3} [d]	11.0×10^{-3}
		254	11.2×10^{-3} [d]	11.2×10^{-3}
	1 (X = I)	313	4.6×10^{-2} [e]	9.2×10^{-2} [f]
		254	6.4×10^{-2} [e]	12.7×10^{-2}
	6	313	3.9×10^{-4} [g]	5.0×10^{-4}
	7	313	6.2×10^{-2} [e]	1.2×10^{-1} 6.0×10^{-1} [h]
Methanol	**1** (X = Cl)	313	1.2×10^{-3} [c]	1.7×10^{-3}
		254	2.5×10^{-3} [c]	3.7×10^{-3}
	1 (X = Br)	313	1.6×10^{-2} [d]	1.6×10^{-2}

[a] Approximately 3×10^{-3} *N* solutions bubbled with nitrogen. [b] Calculated from ϕ_{meas} and the ratio of products formed. [c] Quantum yield for formation of fluoranthene, followed by appearance of its 358-mμ peak. [d] Quantum yield for formation of total products, followed by vpc. [e] Quantum yield for formation of iodine, followed by appearance of its 490-mμ peak. [f] Through an arithmetic error, the ϕ's reported in our earlier communication[1] for **1** (X = I) are in error by a factor of 2. [g] Quantum yield for the formation of the fluoranthene **9**, followed by appearance of its 364-mμ peak. [h] Quantum yield for the conversion of **7** to **1** (X = I).

Table VI. Effect of Solvent on Quantum Yields (ϕ) for Generation of 1-Phenylnaphthalene (**2**) and Fluoranthene (**3**) from 1-(*o*-Chlorophenyl)naphthalene[a]

Solvent	$10^4\phi_2$	$10^4\phi_3$	ϵ[b]	K_H/K_C[c]
Methanol	4.7	12.0	32	0.13
Ethanol	5.0	7.4	24	0.83[d]
Isopropyl alcohol	5.3	5.7	18	2.06[d]
t-Butyl alcohol	1.7	5.5	11	0.15[d]
Ethyl ether	5.8	3.8	4.3	1.66[d]
Benzene	1.5	5.7	2.3	Low
Acetonitrile	1.7	13.6	39	0.09
Acetic acid	0.5	15.8	6.2	0.09
Cyclohexane	3.5	0.8	1.9	1.08
Methylcyclohexane	3.1	0.8	1.9	1.55

[a] Approximately 3×10^{-3} *N* solutions bubbled with nitrogen. [b] Dielectric constant of the solvent at 25°. [c] Rate of abstraction of hydrogen from the solvent by phenyl radicals relative to the rate of abstraction of chlorine from carbon tetrachloride; from the work of R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963). [d] Best estimates of K_H/K_C were based on results of Bridger and Russell for other solvents.

found to be present in the products from photolysis of **1** (X = Cl), but not from **1** (X = Br) or **1** (X = I). This compound was independently synthesized by a known method,[14] and both samples exhibited identical vpc retention times and mass spectral patterns.

Results for the irradiation of 1-(*o*-chlorophenyl)-5-methoxynaphthalene (**6**) in methanol are given in Table IV. As in the benzene solution photolyses, a vpc peak ascribed to 1-phenyl-5-methoxy-8-chloronaphthalene was detected.

Quantum Yields. Quantum yields of disappearance of most of the halophenylnaphthalenes were obtained with two different wavelengths of exciting light. In all cases, the amount of conversion to products was kept to <1.5% since the aromatic products as well as bromine and iodine absorbed at the exciting wavelength. For photolyses of the chloro compounds **1** and **6** the rate of formation of the fluoranthene was followed spectroscopically. The photolysis of the bromo compound **1** (X = Br) was followed by vpc while the iodo compounds were followed by measuring spectroscopically the rate of formation of iodine. From the above data and the ratios of products formed, values of ϕ_D, the quantum yield of disappearance of starting material, were obtained. The results are given in Table V. Surprisingly, compound **1** (X = Cl) was found to photolyze more than 500 times faster than 1-(*p*-chlorophenyl)naphthalene, 1- and 2-chloronaphthalene, or 9-(*o*-chlorophenyl)anthracene. It should be noted that the ϕ_D values reported in Table V in benzene using 254-mμ light are probably in large part the result of photosensitization by benzene. The benzene in these runs absorbs 80–90% of the light.

An examination of the effect of solvent on the quantum yields of product formation revealed a small dependence on solvent polarity and viscosity and a greater dependence on hydrogen donor ability (*cf.* Table VI). A search was made for the possible solvolysis product 1-(*o*-acetoxyphenyl)naphthalene in the acetic acid runs. No vpc peak was found at the position indicated by authentic material prepared by acetylation of 1-(*o*-hydroxyphenyl)naphthalene.

Photosensitization and Quenching. The iodo compound **1** (X = I) reacted readily when excited by sensitizers having triplet energies greater than 60 kcal/mole using 365-mμ light, a wavelength not absorbed by **1**. Measurements were made in benzene solutions 10^{-2} *N* in both the substrate and the sensitizer. The rate of appearance of the 490-mμ peak of I_2 was used to determine the rate of disappearance of substrate. Under these conditions, 4,4′-dimethylbenzophenone, benzophenone, and α-naphthoflavone (E_T = 68.7, 68.5, and 62.0 kcal/mole, respectively) gave ϕ_D's of 7.0, 6.2, and 6.0×10^{-2}, respectively, while β-naphthyl phenyl ketone and biacetyl (E_T = 59.6, 54.9 kcal/mole)[15] gave ϕ_D's of 6×10^{-3} and 2×10^{-3} and fluorenone and fluoranthene (E_T = 53.3 and 52.5 kcal/mole)[15] gave no detectable iodine with **1** (X = I) on irradiation. The bromo and chloro compounds **1** (X = Br and Cl) failed to react detectably under the same conditions when photosensitized with benzophenone, indicating an upper limit for ϕ_D of the sensitized reaction of these two compounds no greater than 1×10^{-5}.

Several quenching experiments were carried out in which ratios of products formed photochemically with and without quenchers present were measured by vpc. The iodo compound **1** (X = I) gave the same product ratio as before (Table II) and with no decrease in quan-

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(14) M. Orchin, *J. Amer. Chem. Soc.*, 70, 495 (1948).

(15) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

tum yield on irradiation with 313-mμ light in benzene containing 1×10^{-2} *N* anthracene ($E_T = 42$ kcal). The quantum yield was corrected for 69% of the incident light which was absorbed by the anthracene. In experiments where 2×10^{-2} *N* perylene ($E_T = 36$ kcal) was added to solutions of the chloro, bromo, and iodo compounds, no change in product ratio was detected on irradiation with 313-mμ light in benzene. Results were complicated, however, by the appearance of some extra peaks in the vpc traces. The perylene, which absorbed 40–50% of the light, did not appreciably affect the quantum yield, ϕ_D.

When the chloro compound (**1**, X = Cl) was irradiated with 300-mμ light in bromobenzene (>98% absorption by **1**) for a period of time sufficient to effect 50–75% reaction in benzene, no reaction could be detected by vpc analysis.

Reactions with Radicals and Radical Traps. When dibenzoyl peroxide is decomposed thermally, phenyl radicals are produced. The radicals may be used to abstract iodine from aryl iodides.[9] When 0.1 *N* dibenzoyl peroxide is decomposed by boiling for 6 hr in the dark in benzene in the presence of 0.1 *N* **1** (X = I), the products **2**, **3**, and **4** are formed in 25, 16, and 59% yield. When a solution of **1** (X = I) of the same concentration is irradiated with 313-mμ light at 80°, the same products are formed in 16, 2, and 82% yield.

Several attempts were made to trap radicals formed on irradiation of the 1-(*o*-halophenyl)naphthalenes **1**. Irradiation of the iodo compound in carbon tetrachloride with 313-mμ light gave 20–30% of the chloro compound (**1**, X = Cl) in addition to **2** and **3**.

Brief irradiation of **1** (X = Cl) in benzene in the presence of 10^{-3} *N* iodine gave with 313-mμ light 0.4% conversion to the iodo compound **1** (X = I) identified by vpc. After longer irradiation, only **2**, **3**, **4**, and **5** were found. The yields of **2**, **3**, and **4** plus **5** were 5, 7, and 88%. To ensure that the products were formed from photoexcited **1** and not photoexcited iodine, an identical solution was irradiated with 450-mμ light (absorbed only by iodine). No reaction occurred.

Discussion

This investigation was conducted in order to determine the reason for the marked dependence of quantum yield and product distribution on the nature of the halogen in the photolysis of haloaromatics, particularly the 1-(*o*-halophenyl)naphthalenes.

The mechanistic conclusions which may be drawn begin with a consideration of the light absorption characteristics of the compounds. The ultraviolet absorption spectra (Table I) of the 1-(*o*-halophenyl)naphthalenes and of 1-phenylnaphthalene are virtually identical, indicating that the halogen has little or no effect on the energy or radiative lifetime of the singlet states formed on excitation. Moreover, the phosphorescence spectra (Table I) of 1-phenylnaphthalene and the three 1-(*o*-halophenyl)naphthalenes show that all four compounds have triplet energies very close to 60 kcal mole. There is, however, a great difference in the ϕ_P/ϕ_F ratios of these four compounds, showing that the rate of intersystem crossing increases markedly with increasing atomic weight of the halogen substituent.

Since 1-(*o*-iodophenyl)naphthalene reacts on sensitization by compounds having $E_T > 60$ kcal, the triplet of **1** (X = I) can be an intermediate in the formation of products. Since the singlet lifetime of **1** (X = I) is extremely short (Table I) and since the quantum yield for the sensitized reaction of this iodo compound is only slightly less than the quantum yield for the unsensitized reaction, it appears that the triplet is the major if not only source of products. On the other hand, neither the bromo nor the chloro analog gives detectable amounts of products on sensitization with benzophenone despite the fact that their triplet energies are identical with that of **1** (X = I). Therefore, it must be concluded that the bromo and chloro compounds react only *via* their excited singlets.

Interestingly, when **1** (X = Cl) is irradiated with 313-mμ light for long periods of time in bromobenzene, no reaction occurs even though **1** absorbs >90% of the light. This may be interpreted as an external heavy atom effect. Such an interpretation is supported by the ratio of phosphorescence to fluorescence quantum yields, ϕ_P/ϕ_F, which for **1** (X = Cl) increases from 3.7 to >30 on going from 3-methylpentane to *n*-butyl bromide as solvent. This observation is similar to that of McClure, McGlynn, Reynolds, Daigre, and Christodoyleas,[16,17] who found that the external heavy atom of propyl bromide is more effective in promoting intersystem crossing in naphthalenes than the internal heavy atom of 1-chloronaphthalene.

The fact that **1** (X = Cl and Br) react photochemically only *via* their excited singlets while **1** (X = I) may react through its triplet suggests homolytic cleavage of the aryl–halogen bond to form the radical **13a**. The energy of the carbon–halogen bonds of iodo-, bromo-, and chlorobenzene is 57.0, 71.0, and 85.6 kcal, respectively.[18] The triplet energy of the halophenylnaphthalenes (60 kcal) should therefore be sufficient to break the carbon–halogen bond of the iodo compound but not that of the chloro or bromo compounds. The singlet energy of **1**, about 90 kcal, is sufficient to break any of the three carbon–halogen bonds. Homolytic cleavage of the C–Cl bond in the naphthyl derivatives is consistent with the failure of 9-*o*-chlorophenylanthracene to undergo photochemical reactions involving loss of chlorine, since the singlet energy of the latter compound (~ 74 kcal mole) is less than that of the aryl C–Cl bond.

Much other evidence indicates that photolysis of aryl iodides in benzene proceeds *via* homolytic cleavage of the carbon–iodine bond to give iodine atoms and aryl radicals.[19] A similar cleavage to give aryl radicals is postulated for aryl bromides.[20] The similarity of the products formed on irradiation of the 1-(*o*-halophenyl)naphthalenes **1** to those obtained above[19,20] also suggests that these reactions are free radical in nature. Thus, the 1-phenylnaphthalene (**2**) and biphenylnaphthalene **4** formed correspond to the reduction and aryla-

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(16) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(17) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodoyleas, *J. Phys. Chem.*, **66**, 2499 (1962).

(18) M. Szwarc and D. Williams, *J. Chem. Phys.*, **20**, 1171 (1952).

(19) For a review of such evidence, see R. K. Sharma and N. Kharasch, *Angew. Chem. Intern. Ed. Engl.*, **7**, 36 (1968); *Angew. Chem.*, **80**, 69 (1968).

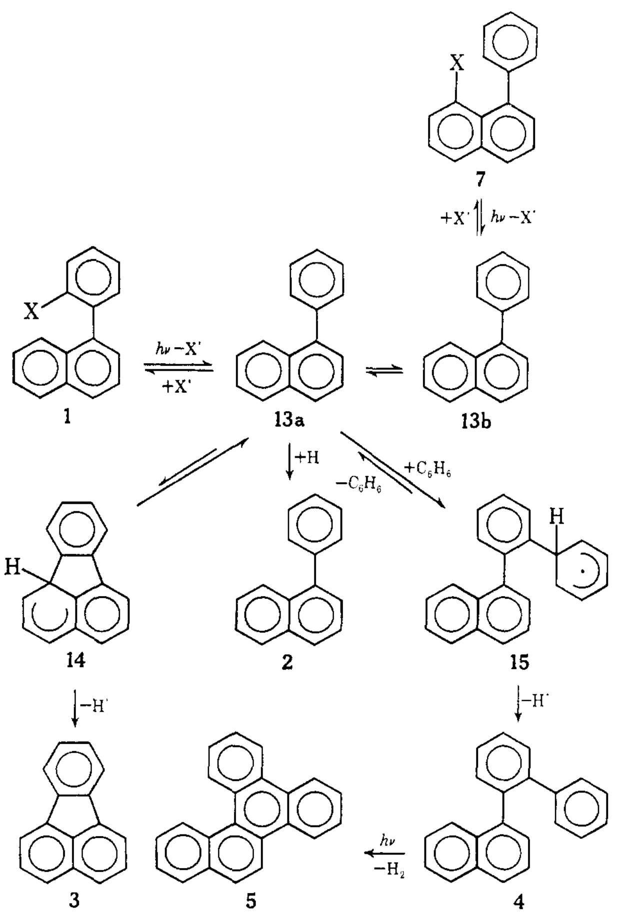
(20) T. Matsuura and K. Omura, *Bull. Chem. Soc., Jap.*, **39**, 944 (1966); N. Kharasch, R. K. Sharma, and H. B. Lewis, *Chem. Commun.*, 1966, 418.

tion products formed on irradiation of iodobenzene in benzene, and the fluoranthene (**3**) formed may be considered as an intramolecular arylation product.[21]

A heterolytic cleavage to give an aryl carbonium ion might be postulated, particularly for the more polar aryl chlorides. Several observations show that the photoreactions of **1** do not proceed *via* such an intermediate. Irradiation of 1-(*o*-chlorophenyl)-5-methoxynaphthalene gives approximately the same yields of intra- and intermolecular arylation products as does irradiation of **1** (X = Cl). If fluoranthene were formed *via* a carbonium ion, the methoxy group should greatly activate the naphthalene ring toward arylation relative to the solvent, benzene,[22] and the yield of fluoranthene should be increased On the other hand, if cyclization. of the radical **13a** is involved, the methoxy substituent would have little activating effect,[23] as is observed. Additionally, when **1** (X = Cl) is irradiated in methanol or acetic acid, only a trace of 1-(*o*-methoxyphenyl)-naphthalene and no acetoxy compound is formed. If reaction of **1** proceeded *via* a carbonium ion, substantial amounts of these two compounds would be expected if cyclization to fluoranthene were not so fast as to preclude this possibility.[24] Finally, while the quantum yield of photochemical formation of fluoranthene is increased in more polar solvents (Table VI), the increase is not so large as would be expected from an ionic intermediate.[25]

The surprisingly high photochemical reactivity of 1-(*o*-chlorophenyl)naphthalene compared to other chloroaromatics such as 1-(*p*-chlorophenyl)naphthalene deserves some comment. It would appear that the unique feature of **1** (X = Cl) is the close proximity of the incipient radical site to the naphthyl group. The formation of the radical **13a** may thus be made more facile through the increased conjugation of the phenyl and naphthalene rings afforded by the decreased steric hindrance between the *ortho* and 8 positions. Alternatively, the radical **13a** may be better protected by the naphthalene ring against attack by the chlorine radical. Since such radical formation and collapse may be a major photochemical process for chloroaromatics, any process hindering the return to starting material should substantially increase the quantum yield of other reactions.

The radical **13a** may undergo several reactions besides the reverse reaction with halogen atoms. It may react with another halogen source to give a new 1-(*o*-halophenyl)naphthalene. The formation of **1** (X = I) on irradiation of **1** (X = Cl) in benzene containing a small amount of iodine and the formation of **1** (X = Cl) on irradiation of **1** (X = I) in carbon tetrachloride both illustrate this process.



The radical **13a** may also rearrange to the radical **13b** *via* a 1,5-hydrogen shift. Good evidence that this reaction and its reverse indeed occur is given by the appearance of **7** on irradiation of **1** (X = I) and by the photoconversion of **7** to **1** (X = I) and its photoproducts (*cf.* Results). Vpc evidence also suggests that the same reactions occur with the chloro and bromo analogs. Failure to observe formation of arylation product formed directly from **7**, *i.e.*, 1,8-diphenylnaphthalene, may be ascribed to the facile interconversion of **13a** and **13b** coupled with the high degree of steric hindrance of the radical **13b**.

The radicals **13a** and **13b** may also undergo photoreduction, abstracting hydrogen from the solvent or some other hydrogen source to give 1-phenylnaphthalene (**2**). As can be seen from Table VI, the quantum yield for, and the relative amount of, photochemical reduction of **1** (X = Cl) is a function of the hydrogen donor ability of the solvent.

The radical **13a** may also take part in two arylation reactions. The first of these is an *intramolecular* cyclization to give the cyclohexadienyl radical **14**. This may in turn be oxidized to fluoranthene (**3**). The second is an *intermolecular* reaction with the solvent benzene to give the radical **15** which would also readily oxidize to yield 1-(2-biphenylyl)naphthalene (**4**).[21] The predominant formation of the intramolecular product, fluoranthene, on irradiation of **1** (X = Cl) in benzene and the predominant formation of the intermolecular arylation products **4** and **5** on irradiation of **1** (X = I) can be explained kinetically. The rearrangement of the radical **13a** to give **14** may be expected to occur much more rapidly than the reaction with benzene to give **15**, since the intramolecular reaction is faster *per se* and because the naphthalene nucleus is known to be about ten times as reactive as benzene toward phenyl

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[21] The only other product found, benzo[*g*]chrysene (**5**), is obviously formed *via* a straightforward photocyclodehydrogenation of **4**; *cf.* F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).

[22] In typical electrophilic substitution reactions, anisole is 10^3–10^9 times as reactive as benzene: L. M. Stock and H. C. Brown, *ibid.*, **82**, 1942 (1960).

[23] Anisole reacts only 1.7 times as fast with phenyl radicals as does benzene; "Advances in Free-Radical Chemistry," Vol. 2, G. H. Williams Ed., Logos Press, London, 1967, p 76.

[24] J. Forrest and S. H. Tucker, *J. Chem. Soc.*, 1137 (1948).

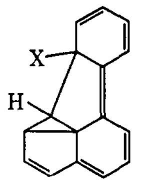
[25] D. F. DeTar and C. Chu, *J. Amer. Chem. Soc.*, **82**, 4969 (1960); A. Streitwieser, Jr., *Chem. Rev.*, **56**, 677 (1956).

radicals.[26] However, the equilibrium between **13a** and **14** should lie further toward **13a** than the equilibrium between **13a** and **15** because the radical **14** is severely strained. This suggests that the cyclohexadienyl radical species formed most rapidly from **13a** will be the fluoranthene precursor **14** (kinetic control). However, in the absence of sufficiently reactive oxidants the cyclohexadienyl radical **15** will become the predominant intermediate (thermodynamic control). Thus, irradiation of **1** (X = Cl) which yields the highly reactive chlorine coradical[27] produces two types of effects which distinguish it from the photolysis of **1** (X = I). First, as reflected in its lower quantum yield, much of the radical **13a** produced reacts rapidly with chlorine radical to revert to starting material. Second, the greater oxidizing ability of the chlorine radical allows it to react with the most rapidly formed radical species, **14**, to produce fluoranthene. Irradiation of **1** (X = I), however, produces the relatively unreactive iodine coradical. The establishment of thermodynamic equilibrium between **13a**, **14**, and **15** will allow the formation of larger amounts of the radical **15** which produces the biphenylnaphthalene **4**. Moreover, the larger size of the iodine radical (steric effect) and the smaller gain in reasonance energy in going from **14** to **3** than in going from **15** to **4** will both favor attack of the iodine radical on **15** rather than **14**. The bromo compound **1** (X = Br) might be expected to, and does, exhibit intermediate behavior.

The importance of the coradical in determining the relative amounts of intra- and intermolecular products formed is also demonstrated by the experiments where the radical **13a** is generated from the iodo compound **1** (X = I) by reaction with thermally generated phenyl radicals. This process normally gives products similar to those formed by the irradiation of aryl iodides.[28] With **1** (X = I), there is an eightfold increase in the amount of fluoranthene over that formed photochemically. This increase is consistent with the greater oxidizing ability of the phenyl radical than the iodine radical.

At high concentrations of **1**, most of the photoreaction occurs in the first portion of the solvent irradiated, and the resultant local concentration of radical species is high. The results given in Table III show that at high concentrations the amount of reduction product **7** is increased at the expense of the oxidation products **3** and **4**. This suggests that at high radical concentrations disproportionative biradical processes such as **13** + **14** → **2** + **3** and **13** + **15** → **2** + **4** occur.

Despite the large amount of evidence consistent with the radical cleavage mechanism, consideration of the bicyclic structure **16**[29] as a possible intermediate in the production of fluoranthene is necessary. This intermediate which has analogy to those found in the photocyclization of stilbenes to phenanthrenes[30] and of diphenylamines to carbazoles[2] would form *via* a singlet, since cyclization of a triplet would involve bonding between unpaired electrons. Thus, the chloro compound **1** (X = Cl), which has a relatively long-lived singlet, would be expected to form much more of the intermediate **16** than either the bromo or iodo analog. Molecular orbital calculations indicate that the coefficients of the wave function at the *ortho* and *peri* positions of 1-phenylnaphthalene are unchanged in sign and value in going from the highest filled to the lowest vacant orbital. Hence ring closure to an intermediate such as **16** would occur in a disrotatory manner to give a *cis* product.[31] However, several observations argue against the intermediacy of **16** in the photogeneration of fluoranthene. First, neither direct nor indirect evidence for **16** at low temperatures could be found. Second, fluoranthene is not formed thermally even though molecular orbital calculations show that thermal cyclization is permitted to the same extent as photochemical cyclization. Third, no fluoranthene is formed when 1-phenylnaphthalene is irradiated in the presence of oxygen and/or iodine, conditions under which intermediates such as **16** are oxidized.[27] Fourth, 1-(*o*-acetoxyphenyl)-naphthalene, in which the acetoxy moiety constitutes a particularly good leaving group from such an intermediate, gives no fluoranthene on irradiation. Fifth, such an intermediate does not explain the failure of the photocyclodehydrohalogenation of 9-*o*-chlorophenylanthracene. Finally, the intermediate **16** does not explain the greatly enhanced rate of formation of the *reduction product*, 1-phenylnaphthalene, relative to the rates of reaction of other chloroaromatics.



16

Experimental Section

Instrumental. Infrared spectra were all obtained on Nujol mulls. Spectra were run on a Perkin-Elmer Model 137 infrared spectrometer. All ultraviolet spectra were run on a Cary Model 15 ultraviolet spectrometer. The luminescence spectrometer and low-temperature cell used for fluorescence and phosphorescence work have been described elsewhere.[32]

All vpc work was done on a F & M Scientific No. 810 chromatograph with a flame ionization detector. All analyses except those for **5** and **11** were done on a 4 ft × 0.25 in. i.d. column packed with 20% Dow Corning QF-1 silicone oil on 70–80 Gas-Chrom CLA. Those for **5** and **11** were run on a 4 ft × 0.25 in. i.d. column packed with 1% General Electric SE-30 silicone rubber on 80–100 Gas-Chrom P. All work was done with T_C = 200°, T_I = 250°, T_D = 250°, and at 50 psi of helium. Approximate retention times in minutes for various compounds were **1** (X = Cl), 5.4; **1** (X = Br), 5.6; **1** (X = I), 7.6; **2**, 3.7; **3**, 12.2; **4**, 10.5; **5**, 4.9; and **7**, 11.4.

Light Sources and Actinometry. Four light sources were used. The first, used for quantum yield determinations at 254 mμ, was a Hanovia low-pressure mercury 12-W, no. 735A-7 lamp, which emits largely 254-mμ light plus 313- and 436-mμ light. The 313-mμ light was removed with a 1,4-diphenylbutadiene filter. The 436-mμ light was removed for actinometric measurements with a Corning no. 9863 filter.

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[26] D. I. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3112 (1961).

[27] G. Briegleb, "Electronen Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961, p 183.

[28] J. F. Bunnett and C. C. Wamser, *J. Amer. Chem. Soc.*, **88**, 5534 (1966).

[29] Six bicyclo[3.1.0]hexane-containing structures of this type can be written.

[30] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964); W. M. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, **85**, 829 (1963).

[31] R. B. Woodward and R. Hoffman, *ibid.*, **87**, 395 (1965).

[32] J. B. Gallivan, J. S. Brinen, and J. G. Koren, *J. Mol. Spectrosc.*, **26**, 24 (1968).

For preparative work at 254 mμ, a Rayonet reactor with RPR 2537-Å lamps was used. About 94% of the light absorbed by the halophenylnaphthalenes was at 254 mμ.

For quantum yield determinations at 313 mμ, a Hanovia medium-pressure 100-W no. 16A-13 lamp was used. The 313-mμ line was isolated using a Corning no. 9863 filter and a 1-cm thick solution of 8×10^{-4} *N* aqueous potassium chromate.

For most preparative work at 313 mμ, the same lamp and filter system was used. All such work is designated as being at 313 mμ.

For runs involving the chloro compounds, rates of photoreaction with the above Hanovia lamp were very low. In many cases the more intense Rayonet reactor with RPR 3000-A° bulbs was used instead. All such work is designated as being at 300 mμ, although the lamp output is strong from 280 to 320 mμ. Calibration of the lamps for quantum yield studies was done by the ferrioxalate method of Hatchard and Parker.[33]

Synthesis. 1-(*o*-Chlorophenyl)naphthalene (1, X = Cl). The compound was synthesized in 18% over-all yield by the method of Johnson and Waters.[8] The product, mp 58–59° (lit. mp 60–61°), showed strong peaks in the infrared at 758 cm^{-1} (*ortho*-disubstituted benzene) and 780 and 802 cm^{-1} (1-substituted naphthalene). The ring–halogen band appeared at 1050 cm^{-1}.

1-(*o*-Bromophenyl)naphthalene (1, X = Br). To 25 g (0.134 mole) of *o*-bromobenzaldehyde in 150 ml of ether was added dropwise with stirring 0.147 mole of 3-phenylpropylmagnesium bromide in 200 ml of ether. The mixture was refluxed 1 hr, cooled, and treated with saturated ammonium chloride solution. The ether layer was separated and evaporated to give an oil. Unreacted aldehyde was removed by treatment with Girard's reagent in hot ethanol–acetic acid. The reaction mixture was poured into ether and water, and the ether layer was separated. Evaporation gave 32.0 g (78%) of **1-(*o*-bromophenyl)-4-phenylbutanol** as a nondistillable oil. This was used without further purification.

A mixture of 32.0 g (0.11 mole) of 1-(*o*-bromophenyl)-4-phenylbutanol, 110 g of phosphoric acid, and 80 g of sulfuric acid was heated on a steam bath for 15 min. The cooled mixture was poured into 500 ml of ice–water to give a gummy precipitate. This was dissolved in ether, washed with sodium bicarbonate solution, and dried. Evaporation gave 22 g (77%) of **1-(*o*-bromophenyl)-1,2,3,4-tetrahydronaphthalene** as a pale yellow oil.

Anal. Calcd for $C_{16}H_{15}Br$: C, 66.91; H, 5.25; Br, 27.82. Found: C, 66.79; H, 5.21; Br, 28.07.

A mixture of 20 g (0.07 mole) of 1-(*o*-bromophenyl)-1,2,3,4-tetrahydronaphthalene and 4.5 g (0.14 g-atom) of sulfur was heated to 260° for 30 min, and then to 280° for 10 min. The mixture was dissolved in hexane and then concentrated to give 14.7 g of an oily solid. This was sublimed and then recrystallized twice from isopropyl alcohol to give 12.0 g (61%) of **1-(*o*-bromophenyl)naphthalene** as colorless crystals, mp 89–91.5°.

Anal. Calcd for $C_{16}H_{11}Br$: C, 67.86; H, 3.91; Br, 28.22; mol wt, 283. Found: C, 68.03; H, 4.18; Br, 28.24; *m/e* 283.

The infrared spectrum showed strong aromatic bands at 758, 780, and 801 cm^{-1}. The ring–halogen band appeared at 1027 cm^{-1}.

1-(*o*-Iodophenyl)naphthalene (1, X = I). From 36 g (0.15 mole) of *o*-iodobenzaldehyde[34] and 0.16 mole of 3-phenylpropylmagnesium bromide, the reaction and work-up run as above, was obtained 43 g (81%) of crude **1-(*o*-iodophenyl)-6-phenylbutanol.** A mixture of 21 g (0.06 mole) of butanol, 70 ml of phosphoric acid, and 28 ml of sulfuric acid, treated as before, gave 16 g (80%) of **1-(*o*-iodophenyl)-1,2,3,4-tetrahydronaphthalene** as a light yellow oil.

Anal. Calcd for $C_{16}H_{13}I$: C, 57.50; H, 4.52; I, 37.97. Found: C, 57.96; H, 4.94; I, 37.62.

Dehydrogenation of 10 g (0.03 mole) of the tetrahydronaphthalene with 2.0 g of sulfur and work-up as above gave 6.6 g (68%) of **1-(*o*-iodophenyl)naphthalene,** mp 109–111°.

Anal. Calcd for $C_{16}H_{11}I$: C, 58.21; H, 3.33; I, 38.43; mol wt, 330. Found: C, 58.03; H, 3.51; I, 38.15; *m/e* 330.

The infrared spectrum showed strong aromatic bands at 760, 782, and 802 cm^{-1}. The ring–halogen band appeared at 1013 cm^{-1}.

Benzo[*g*]chrysene (5). A solution of 200 mg of 1-(2-biphenylyl)-naphthalene and 20 mg of iodine in 200 ml of cyclohexane was irradiated with 254-mμ light for 15 hr. The solvent was evaporated and the residue chromatographed on alumina. After the first few fractions, which contained much starting material, crude benzo[*g*]-chrysene was eluted with petroleum ether (bp 30–60°)–ether. The compound was recrystallized twice from acetic acid to give 22 mg of benzo[*g*]chrysene, mp 114–116° (lit.[35] mp 114–115°). The ultraviolet spectrum in ethanol with peaks at 371 mμ (log ε 2.46), 353 sh (2.89), 333 (3.93), 319 (4.06), 307 (4.04), 286 (4.80), 276 (4.79) matches exactly that reported by Clar.[36]

1-(*o*-Chlorophenyl)-5-methoxynaphthalene (6). To 0.10 mole of *o*-chlorophenylmagnesium iodide in 60 ml of ether was added with stirring 16.4 g (0.10 mole) of 5-methoxytetralone in 60 ml of benzene. The mixture was refluxed 3 hr and then decomposed with saturated ammonium chloride solution. The organic layer was decanted and evaporated to yield a viscous oil. This was heated on a steam bath for 25 min with 15 ml of acetic anhydride and then distilled to give 9.2 g (34%) of **1-(*o*-chlorophenyl)-5-methoxy-3,4-dihydronaphthalene,** bp 176–180° (0.02 mm). To 9.0 g (0.03 mole) of the above compound was added 1.06 g (0.033 mole) of sulfur. The mixture was heated to 250–280° for 30 min. After evolution of hydrogen sulfide ceased, the mixture was cooled to leave a brown mass. This was distilled from the same flask to give a light yellow oil, bp 146–148° (0.01 mm). The oil crystallized from methanol and was recrystallized twice to give 5.98 g (68%) of **1-(*o*-chlorophenyl)-5-methoxynaphthalene,** mp 87–89°.

Anal. Calcd for $C_{17}H_{13}ClO$: C, 76.00; H, 4.88; Cl, 13.20. Found: C, 76.09; H, 4.91; Cl, 13.01.

The infrared spectrum of **6** showed strong peaks at 760 and 782 cm^{-1} (*ortho*-disubstituted phenyl and 1,5-disubstituted naphthalene) and 1035, 1243, and 1255 cm^{-1} (aryl ether).

1-Iodo-8-phenylnaphthalene (7). A mixture of 15 g (0.060 mole) of 1-bromo-8-nitronaphthalene,[37] 30 g (0.147 mole) of iodobenzene, and 8 g of copper bronze[38] was heated with stirring in a sealed tube to 240° for 3 hr. The mixture was cooled, dissolved in benzene, filtered, and evaporated. Chromatography of the residue on 300 g of alumina gave crude product. This was recrystallized twice from methanol to give 5.20 g (35%) of **1-nitro-8-phenylnaphthalene,** mp 106–108°.

Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.45; N, 5.62. Found: C, 76.94; H, 4.47; N, 5.50.

The above compound was reduced with iron powder and hydrochloric acid according to the method of Hazlett and Dornfeld[39] to give 93% of **1-amino-8-phenylnaphthalene hydrochloride,** mp 155–157°. An analytical sample, mp 165–170° dec, was obtained on recrystallization from methanol.

Anal. Calcd for $C_{16}H_{14}NCl$: C, 75.17; H, 5.52; N, 5.48. Found: C, 75.13; H, 5.39; N, 5.66.

In 20 ml of hydrochloric acid and 80 ml of water was dissolved 3.00 g (0.010 mole) of the above hydrochloride. The solution was cooled to 0° and diazotized by slow addition of 1.50 g of sodium nitrite. The mixture was stirred 15 min and then poured into an ice-cold solution of 20 g of sodium iodide in 100 ml of water. The mixture was stirred for 2 hr while the temperature was slowly raised to 25°. Sodium bisulfite was added to remove iodine, and the mixture then extracted with benzene. The benzene solution was washed with water and dried, and the solvent removed. The residue was chromatographed on alumina and the product recrystallized from methanol to give 0.73 g (19%) of **1-iodo-8-phenylnaphthalene** as white crystals, mp 65.0–65.5°.

Anal. Calcd for $C_{16}H_{11}I$: C, 58.20; H, 3.36; mol wt, 330. Found: C, 58.04; H, 3.03; *m/e* 330.

The infrared spectrum showed strong bands for 1,8-disubstituted naphthalene and monosubstituted benzene at 696, 754, 767, and 818 cm^{-1}. A strong band at 958 cm^{-1} is assigned to the iodine–ring interaction.

9-(*o*-Chlorophenyl)anthracene. A solution of 4 g of anthracene, 3.1 g of *o*-chloroaniline, and 4.5 g of amyl nitrite in 100 ml of benzene was heated to reflux for 18 hr. The solution was evaporated at reduced pressure, and the residue was sublimed. The yellow sublimate was recrystallized from benzene to remove most of the unreacted anthracene. The mother liquor was concentrated and

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(33) C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953); C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956).

(34) W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 487 (1941).

(35) C. L. Hewett, *ibid.*, 193 (1938).

(36) E. Clar, "Polycyclic Hydrocarbons," Vol. 1, Academic Press, London, 1964, p 266.

(37) A. Sieglitz, H. Troester, and P. Boehme, *Ber.*, **95**, 3013 (1962).

(38) United States Bronze Powder Works copper bronze powder C-118, activated by the method of A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., Ltd., London, 1961, p 192.

(39) S. E. Hazlett and C. A. Dornfeld, *J. Amer. Chem. Soc.*, **66**, 1781 (1944).

chromatographed on alumina. The appropriate fractions were combined and recrystallized from benzene–methanol to give 50 mg (0.8%) of white crystals, mp 128–133° (lit.[9] mp 140°).

Anal. Calcd for $C_{20}H_{13}Cl$: C, 83.18; H, 4.54. Found: C, 83.26; H, 4.50.

The compound showed in the infrared strong aromatic bands at 738 and 752 cm^{-1} (*ortho*-disubstituted benzene) and 895 cm^{-1} (pentasubstituted benzene). The ring-halogen band appeared at 1054 cm^{-1}. The ultraviolet spectrum matched that reported in the literature.[9]

1-Phenyl-5-methoxynaphthalene (8). In the same manner as that used to prepare 1-(*o*-chlorophenyl)-5-methoxy-3,4-dihydronaphthalene, **1-phenyl-5-methoxy-3,4-dihydronaphthalene,** bp 145–150° (0.05 mm), was prepared in 74% yield from phenylmagnesium bromide and 5-methoxytetralone. Dehydrogenation with sulfur as before followed by recrystallization from methanol gave **1-phenyl-5-methoxynaphthalene,** mp 80–83°, in 68° yield. An analytical sample, mp 82–83°, was prepared by recrystallization from hexane.

Anal. Calcd for $C_{17}H_{14}O$: C, 87.14; H, 6.02. Found: C, 87.04; H, 5.99.

The infrared spectrum showed strong peaks at 706, 766, and 784 cm^{-1} (1,5-disubstituted naphthalene and monosubstituted benzene) and 1086 and 1233 cm^{-1} (aromatic ether). The ultraviolet spectrum in ethanol displayed peaks at 219 mμ (log ϵ 4.62), 235 (4.52), 299 (3.99), 309 sh (3.94), 314 sh (3.89), and 323 (3.78).

3-Methoxyfluoranthene (9). A solution of 200 mg of **6** in 100 ml of methanol was irradiated with 254-mμ light for 18 hr. The brilliantly fluorescent solution was evaporated and chromatographed on alumina. The yellow, fluorescent fractions were combined, evaporated, and recrystallized from methanol to give 95 mg of **3-methoxyfluoranthene** as lemon-yellow plates, mp 160–161° (lit.[37] mp 156°). The ultraviolet spectrum in methanol matched that reported in the literature.[37]

5-Methoxy-1-(2-biphenylyl)naphthalene (10). Using the same method as for the preparation of 1-(2-biphenylyl)naphthalene,[11] **5-methoxy-1-(2-biphenylyl)-3,4-dihydronaphthalene** was prepared in 88% yield from 2-biphenylyllithium and 5-methoxynaphthalene. Dehydrogenation with sulfur at 250–280° followed by chromatography on alumina gave a very intractable oil. This finally crystallized from ethanol to give a 55% yield of **5-methoxy-(4-biphenylyl)naphthalene,** mp 98–99°.

Anal. Calcd for $C_{23}H_{18}O$: C, 88.99; H, 5.84. Found: C, 88.82; H, 5.75.

The infrared spectrum showed strong peaks at 702, 746, 766, 787, 1080, and 1255 cm^{-1}. The ultraviolet spectrum in ethanol displayed peaks at 223 mμ sh (log ϵ 4.70), 234 sh (4.65), 290 sh (3.88), 301 (3.97), 310 sh (3.92), and 324 (3.74).

1-(*o*-Acetoxyphenyl)naphthalene. To 1.4 g of **1-(*o*-hydroxyphenyl)naphthalene**[14] in 1 ml of acetic anhydride was added 1 drop of concentrated sulfuric acid. The solution became warm, and after 5 min, it was heated gently on a steam bath for an additional 5 min. The solution was poured into water and extracted with ether–benzene. The organic layer was dried, concentrated, and distilled at reduced pressure to give 1.1 g (67%) of 1-(*o*-acetoxyphenyl)naphthalene as a thick, uncrystallizable oil, bp 126–135° (0.1 mm).

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.40; H, 5.35.

The compound showed strong aromatic peaks in the infrared (neat oil) at 758 cm^{-1} (*ortho*-disubstituted benzene) and 780 and 804 cm^{-1} (1-substituted naphthalene). The acetoxy group absorbed at 1765, 1365, and near 1200 cm^{-1}.

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The Entropies of Dissociation of Some Moderately Strong Acids

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Abstract: The dissociation constants of seven moderately strong ($0.5 < pK_a < 1.4$) uncharged acids have been measured as a function of temperature. The acids were chosen to serve as models for the interpretation of $\Delta S^\ddagger$ values derived from rates. A simplified method for the determination of these dissociation constants is shown to give results of more than sufficient accuracy when applied to those few moderately strong acids for which classically determined values exist. The near-zero values of $\Delta S°$ measured for the ionization of certain of the acids are discussed from the viewpoints of their implications concerning changes in solvent structure accompanying the activation process in solvolytic reactions and concerning the general use of equilibrium $\Delta S°$ values as models for interpreting $\Delta S^\ddagger$ values. The parameters found for dissociation at 25° are (given in order for each acid are pK_a, $\Delta H°$ in kcal $mole^{-1}$, and $\Delta S°$ in cal deg^{-1} $mole^{-1}$): Cl_2FCCO_2H, 0.46, −1.4, −7; F_3CCO_2H, 0.50, 0.4, −1; Cl_3CCO_2H, 0.515, 0.28, −1.4; $^+H_3NSO_3^-$, 0.998, 0.41, −3.2; $(CO_2H)_2$, 1.30, −0.8, −9; F_2CHCO_2H, 1.34, −2.0, −13; Cl_2CHCO_2H, 1.36, −1.9, −12.

Owing to the difficulties encountered in applying the classical potentiometric, conductometric, and spectrophotometric methods for the precise measurement of pK_a values to acids with pK_a less than 2, the standard thermodynamic parameters for ionization of very few such acids have been reported. This is unfortunate in view of the use of acid ionization equilibria as models for the interpretation of thermodynamic parameters for activation, particularly $\Delta S^\ddagger$ [1–3] and $\Delta C_p^\ddagger$.[3] This unavailability of data has required that the values of $\Delta S°$ and $\Delta C_p°$ for the ionization of weak acids, such as acetic, be compared to values of $\Delta S^\ddagger$ and $\Delta C_p^\ddagger$ for ionogenic reactions in which the leaving groups are the anions of acids which bear little structural resemblence to the anion of the model acid. Such comparisons invoke the generalization[4] that all ionizations of un-

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