—The hydrochloride of VI (1.00 g.) was dissolved in boiling water (25 ml.), and the cooled mixture was extracted with ether (10 ml.). The aqueous solution was clarified with Norit, brought to a volume of 50 ml., treated with glacial acetic acid (1.0 ml.), cooled to 5°, and finally treated dropwise with stirring with a solution of 2.2 g. of sodium nitrite in 22 ml. of water. After the addition the mixture was allowed to warm to room temperature and to stand for 1 hr., then was made alkaline with potassium hydroxide and extracted with ether. The extract was washed, dried over magnesium sulfate, and stripped of solvent to yield 0.87 g. of oil which was chromatographed (benzene) on 50 g. of neutral alumina (Activity II), affording 0.147 g. of yellow oil which partially crystallized and whose infrared spectrum was similar to that of tri(*p*-anisyl)ethylene. Elution with benzene-ether (4:1) yielded 0.59 g. (65%) of 1,2,2-tri(*p*-anisyl)-ethanol. Final elution with methanol yielded 0.151 g. of solid which was not characterized. Recrystallization of the alcohol fraction from *n*-hexane-chloroform (2:1) yielded pure 1,2,2-tri(*p*-anisyl)ethanol, m.p. 107–109° in agreement with the reported value.[30]

A similar procedure was employed, using proportional quantities, in the deamination of 7.7 g. of the above 1,2,2-tri(*p*-anisyl)ethylamine-1-C^{14} hydrochloride, affording 2.67 g. (38%) of purified 1,2,2-tri(*p*-anisyl)ethanol-1,2-C^{14} (X), m.p. 108–110.5°, specific radioactivity 2.583 ± 0.002 mc./mole.

Degradation of 1,2,2-Tri(*p*-anisyl)ethanol-1,2-C^{14} (X).—The above X (2.55 g.) was oxidized to 2.53 g. (99%) of radioactive *p*-anisyl di(*p*-anisyl)methyl ketone by the method of Sarett and co-workers,[20] using chromic acid (2.30 g.) and pyridine (23 ml.). The crude ketone, whose infrared spectrum was identical with that of an authentic sample, was degraded with sodium ethylate as described above, yielding 0.66 g. (62%) of crude *p*-anisic acid and 1.45 g. (91%) of crude di(*p*-anisyl)methane. The purified *p*-anisic acid had m.p. 180–182° and a radioactivity assay of 2.083 ± 0.003 mc./mole. The recrystallized di(*p*-anisyl)methane had m.p. 50.5–52° and a radioactivity of 0.432 ± 0.0002 mc./mole.

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[30] K. Sisido, K. Okano, T. Isida, and H. Nozaki, *J. Am. Chem. Soc.*, **77**, 3580 (1955).

Partial Rate Factors for Nitration of Fluoranthene[1]

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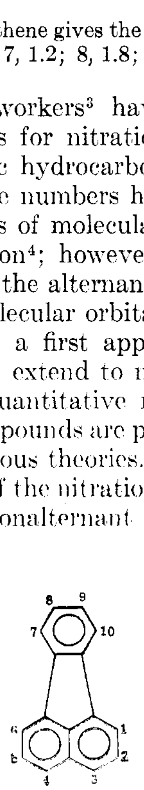
Nitration of fluoranthene gives the following partial rate factors relative to a 1-naphthalene position: in acetic anhydride at 0°: 1, 0.7; 3, 2.9; 7, 1.2; 8, 1.8; in acetic at 50°: 1, 0.3; 3, 8.1; 7, 0.6; 8, 2.7.

Dewar and co-workers[3] have determined the partial rate factors for nitration of a number of polycyclic aromatic hydrocarbons in acetic anhydride at 0°. These numbers have been useful for testing applications of molecular orbital theory to aromatic substitution[4]; however, the hydrocarbons studied were all of the alternant type for which all of the common molecular orbital reactivity indices are interrelated to a first approximation.[4] Such limitation does not extend to nonalternant hydrocarbons; hence, quantitative reactivity measurements for such compounds are particularly valuable for testing the various theories. We report the results of our study of the nitration of fluoranthene, I, a benzenoid but nonalternant aromatic hydrocarbon.



I

The nitration of fluoranthene has long been known to give predominantly 3-nitrofluoranthene, 3-II[5]; this isomer can be isolated readily in good yield.[6] von Braun and Manz[7] proved the presence of 8-nitrofluoranthene, 8-II, in the crude nitration product; however, only relatively recently has this isomer been isolated and characterized.[8] During the preliminary phases of our work, spectral comparisons of the product of nitration in acetic anhydride with 3- and 8-II indicated the presence of other isomers. Repeated chromatography of the nitration product on alumina eventually afforded two additional isomers in pure state, m.p. 144–144.5° and 150–151°.

Of the five possible mononitrofluoranthenes, four were known prior to our work. 1-Nitrofluoranthene 1-II, m.p. 151–153°, has been prepared by Campbell and Wilshire.[9] 2-Nitrofluoranthene, 2-II,

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[1] Supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, by a grant and by Contract No. AF-49(638)-105. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] Alfred P. Sloan Fellow, 1958–1962.

[3] Summarized in M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

[4] For a detailed review see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, 1961, Chap. 11.

[5] J. von Braun and G. Manz, *Ann.*, **488**, 111 (1931).

[6] R. J. Garascia, E. F. Fries, and C. Ching, *J. Org. Chem.*, **17**, 226 (1952).

[7] J. von Braun and G. Manz, *Ann.*, **496**, 170 (1932).

[8] M. C. Kloetzel, W. King, and J. H. Menkes, *J. Am. Chem. Soc.*, **78**, 1165 (1956).

[9] N. Campbell and J. F. K. Wilshire, *J. Chem. Soc.*, 867 (1954). Note that these authors use a different numbering system for fluoranthene and call this isomer the 2-nitro compound. This name was picked up by *Chemical Abstracts* where the compound is listed erroneously as "2-nitrofluoranthene" in both abstract and indices.

m.p. 153–153.5°, has been prepared by Kloetzel, King, and Menkes.[8] Mixture melting points and infrared comparisons with an authentic sample of 2-II kindly supplied by Professor Kloetzel showed that neither of our nitration products was the 2-isomer.

Both nitration products were hydrogenated to the corresponding aminofluoranthenes, III. 1-Aminofluoranthene, 1-III, has been synthesized both by Campbell and Wilshire, m.p. 134–136°,[9] and by Bergmann and Orchin,[10] m.p. 133–134°. The amine from the higher melting nitration product, m.p. 131.5–132.5°, did not depress an authentic sample of 1-III, kindly supplied by Professor Orchin. The amine from the lower melting nitration product had m.p. 126–128.5° and did depress authentic 1-III. By elimination, the lower melting nitration product clearly is the hitherto unknown 7-isomer, 7-II. All of the mononitrofluoranthenes are now known and may be characterized by differences in the infrared spectrum particularly in the 10–12-μ region (Table I).

TABLE I

INFRARED SPECTRA OF NITROFLUORANTHENES

Position of nitro	Exp. m.p., °C.	M.p., °C. (lit.)	Infrared bands, μ[a]
1	150–151	151–153[9]	10.88(w), 11.94(s), 12.40
2	157–160[b]	153–153.5[8]	11.17 (broad shoulders at 11.35 and 11.45)
3	160–162.5	159–160[5]	10.75, 11.71, 12.17
7	144–144.5		11.74, 12.07, 12.27
8	162–164	158–160[8]	11.11, 11.52, 11.87, (w), 12.12 (s)

[a] Bands are of medium intensity except where indicated as (w) weak, or (s) strong. [b] Sample provided by Professor Kloetzel.

Fluoranthene was nitrated in acetic anhydride at 0° and in acetic acid at 50° under conditions that gave incomplete nitration. The product was separated both from unchanged fluoranthene and from small amounts of red oxidation products by a preliminary chromatography on alumina. The resulting mixture of mononitrofluoranthenes was then rechromatographed and eluted in two portions. The infrared spectrum of each portion was taken in chloroform solution and compared with similar spectra of the pure isomers. These spectra demonstrate the absence of significant amounts of 2-II and reduce the analytical problem to a four-component system. The intensities at seven selected wave lengths gave an overdetermined system for which the least squares solution was obtained using an IBM 704 computer.[11] The analyses for the two portions were added to give the composition of each nitration mixture (Table II).

TABLE II

NITRATION PRODUCTS OF FLUORANTHENE

Position	Per cent Ac$_2$O, 0°	Per cent AcOH, 50°
1	11.1 ± 3.3	2.3 ± 1.5
3	43.5 ± 5.8	69.6 ± 2.7
7	18.4 ± 3.9	5.0 ± 1.9
8	27.0 ± 5.8	23.1 ± 2.7

To convert the orientation values found to partial rate factors, competitive nitrations were run between fluoranthene and naphthalene. Known mixtures of naphthalene and fluoranthene were nitrated with insufficient nitric acid in acetic acid at 50° and in acetic anhydride at 0°. The reaction mixtures were isolated and analyzed by gas chromatography. Peak areas were related by standards to the relative amounts of unreacted naphthalene and fluoranthene and of nitronaphthalenes and nitrofluoranthenes present. The relative rate is given by,[12]

$$\frac{k_F}{k_N} = \frac{k_{\text{fluoranthene}}}{k_{\text{naphthalene}}} = \frac{\log\,(1 - M_{\text{nitrofluoranthenes}}/M^{\circ}_{\text{fluoranthene}})}{\log\,(1 - M_{\text{nitronaphthalenes}}/M_{\text{naphthalene}})}$$

in which M refers to moles of subscript compound. Results are shown in Table III.

TABLE III

COMPETITIVE NITRATIONS OF NAPHTHALENE AND FLUORANTHENE

Solvent	Temp., °C.	Fluoranthene at start ($M°$) 10^3 moles	Naphthalene at start ($M°$) 10^3 moles	k_F/k_N	
AcOH	50°	4.71	13.6	5.7, 5.9	5.5 ± .3
		4.62	21.1	5.1, 5.4	
Ac$_2$O	0°	4.71	13.15	3.4, 2.9	3.0 ± .5
		4.80	19.8	2.2, 3.6	

Finally, in order to derive partial rate factors with respect to a given position in naphthalene, the relative amounts of nitration at the α- and β-positions were determined by gas chromatography. The results obtained from the several runs are summarized in Table IV.

Our results in acetic anhydride are in fair agreement with those obtained by Dewar and Mole[13] using ultraviolet spectral analyses: 0°, $k_\beta/k_\alpha = 0.10$; 45°, $k_\beta/k_\alpha = 0.13$.

Using our combined values we derive the sets of partial rate factors shown in Table V. The partial

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(10) E. Bergmann and M. Orchin, *J. Am. Chem. Soc.*, **71**, 1917 (1949).

(11) We have m equations in n unknowns: $\sum_{j=1}^{n} a_{ij}X_j = b_i$, in which a_{ij} is the spectral intensity of isomer X_j at the ith wave length, and b_i is the intensity of the unknown mixture at the ith of m wave lengths, $m > n$. For the equivalent matrix equation, $\mathbf{AX} = \mathbf{B}$, the desired solution is well known to be $\mathbf{X} = (\mathbf{A'A})^{-1}\mathbf{A'B}$. We are indebted to J. I. Brauman for performing the calculations and for writing the program which embodied standard library matrix arithmetic subroutines.

(12) M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3576 (1956).

(13) M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1441 (1956).

TABLE IV

ORIENTATION IN NITRATION OF NAPHTHALENE

Solvent	Temp., °C.	$k\beta/k\alpha$	Average
AcOH	50	0.058, 0.063, 0.073 0.055, 0.069, 0.053	0.062 ± 0.006
	100	0.082, 0.082, 0.083, 0.091	0.084 ± 0.003
Ac_2O	0	0.108, 0.112, 0.110, 0.119, 0.110	0.112 ± 0.003
	50	0.124, 0.123, 0.124, 0.129	0.125 ± 0.002

rate factors are given relative to a 1-naphthalene position.

TABLE V

REACTIVITY OF FLUORANTHENE AND NAPHTHALENE

Hydrocarbon	Position	$f^N_{Ac_2O}$[a] 0°	f^{N+}_{AcOH}[a] 50°	q_r[b]	L_r^{+}[b]	F_r[b]
Naphthalene	1	1	1	1	2.299	0.453
	2	0.110	0.062	1	2.480	0.404
Fluoranthene	1	0.7	0.3	0.947	2.466	0.453
	2	...	...	1.005	2.503	0.398
	3	2.9	8.1	0.959	2.341	0.470
	7	1.2	0.6	0.997	2.371	0.438
	8	1.8	2.7	1.008	2.435	0.409

[a] Partial rate factor relative to 1-naphthalene. [b] Summarized in ref. 4.

Inspection of Table V reveals immediately that acetic acid is a more selective solvent than is acetic anhydride. The relationship is shown clearly by a plot of log $f^N_{Ac_2O}$ *vs.* log f^N_{AcOH} (Fig. 1). Despite the low precision of some of the fluoranthene data in acetic acid, the plot shows a satisfactory linear correlation with a slope of about 1.3. The difference is not large but can make a substantial difference in preparative chemistry. As exemplified by our results with fluoranthene, acetic acid is the solvent of choice when only the nitration product at the most reactive position is desired; acetic anhydride is the solvent to use if one desires to isolate products of reaction at less reactive positions. This selectivity difference does not appear to be generally recognized; it is well known that the use of acetic anhydride gives high *ortho*-substitution with compounds such as anisole and acetanilide,[14] but the special mechanisms apparently operating with these compounds are probably not significant with aromatic hydrocarbons.

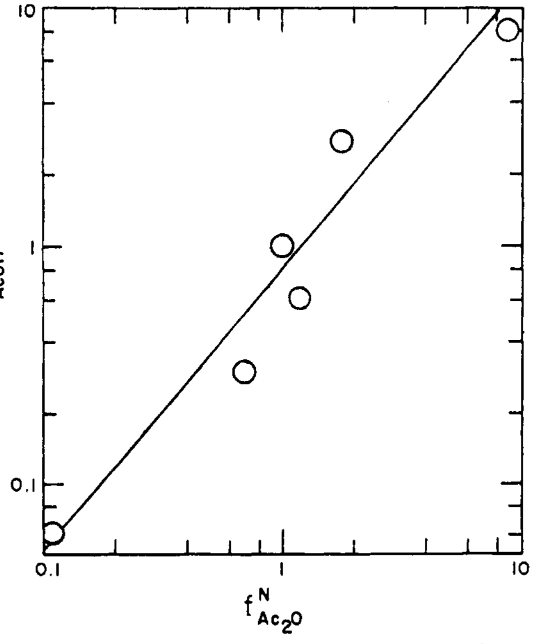

Fig. 1.—A log-log comparison plot of partial rate factors for nitration of naphthalene and fluoranthene in acetic anhydride and in acetic acid.

Although a more detailed discussion of the application of molecular orbital theory to these results is presented elsewhere,[15] some pertinent comments are appropriate here. Among the most common criteria of reactivity are the free valence, *F*, the electron density, *q*, and the cation localization energy, L^+.[4] Of these criteria, the cation localization energy comes closest to predicting the correct order of reactivities in fluoranthene: calculated, 3>7>8>1>2; experimental, 3>8>7>1>2. Only the 8-position is out of line. More serious, however, is the failure of this method in comparing relative rates with naphthalene. All fluoranthene positions are predicted by the localization energies to be less reactive than a naphthalene-1 position, whereas, experimentally, several fluoranthene positions are more reactive than the standard. The application of the ω-technique is discussed elsewhere and brings the calculations closer in line with experiment.[15]

Experimental

Nitration of Fluoranthene in Acetic Anhydride.—To a suspension of 101 g. (0.5 mole) of fluoranthene in 500 ml. of acetic anhydride maintained at 0–5° was added a mixture of 25 ml. of concentrated nitric acid (0.385 mole) in 150 ml. of cold acetic anhydride over a period of 1 hr. A yellow solid gradually replaced the white fluoranthene. After 2 hr. at 0°, the mixture was warmed until the solid dissolved. Slow cooling and seeding with 3-nitrofluoranthene gave 30 g. of solid in two crops. The filtrate was diluted with water and allowed to stand until the acetic anhydride had hydrolyzed. The precipitated solid was taken up in carbon tetrachloride and chromatographed repeatedly on AG-7 neutral alumina using pentane, hexane, benzene, and chloroform as eluents at various stages. Ultimately, two other nitrofluoranthenes were obtained in addition to 3- and 8-nitrofluoranthene. In the absence of infrared spectra of the new isomers the chromatographic separation was tedious and inefficient. In retrospect, it appears that separation may be facilitated by making use of the higher solubility of the new isomers by a prior extraction with pentane or hexane. The additional isomers are identified as the 1- and 7-nitrofluoranthenes. The order of elution from alumina is 1, 7, 3, 8. No 2-nitrofluoranthene was detected.

The different nitrofluoranthenes have similar melting points; identification and differentiation may be accomplished more readily by the infrared spectra. These prop-

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(14) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths, London, 1959, Chap. 4 and 5.

(15) A. Streitwieser, Jr., J. I. Brauman, and J. B. Bush, to be published.

erties are summarized in Table I. Mixture melting points of 1- and 7-nitrofluoranthene with each other and with each of the other three mononitrofluoranthenes depressed. As a new compound, a sample of 7-nitrofluoranthene was analyzed.[16]

Anal. Calcd. for $C_{16}H_9NO_2$: C, 77.73; H, 3.64; N, 5.67. Found: C, 77.45; H, 3.72; N, 5.70.

1-Aminofluoranthene.—A solution of 100 mg. of 1-nitrofluoranthene in 15 ml. of ethanol was hydrogenated at atmospheric pressure with palladium-on-charcoal and took up 105% of the theoretical hydrogen. The amine was precipitated with water but purification was difficult—solutions colored rapidly. Recrystallization from hexane finally yielded 15 mg. of yellow needles, m.p. 131.5–132.5°. A mixture with an authentic sample kindly supplied by Professor Orchin, m.p. 132.5–135.5°, melted at 131–135.5°.

A second hydrogenation with 150 mg. of 1-nitrofluoranthene was carried out in benzene. After filtering off the catalyst, acetic anhydride was added. After warming for several minutes, 110 mg. of fine white needles of 1-acetylaminofluoranthene was obtained, m.p. 257–258° (lit.[9] 254–255°).

7-Aminofluoranthene.—A solution of 209 mg. of 7-nitrofluoranthene in ethanol was hydrogenated as above. Crystallization of the product from benzene-hexane gave 120 mg. of yellow-green crystals, m.p. 126–128.5°. A mixture m.p. with authentic 1-aminofluoranthene was depressed.

Anal.[16] Calcd. for $C_{16}H_{11}N$: N, 6.45. Found: N, 6.29.

Partial Rate Factors in Nitration.—A solution of 1.01 g. of fluoranthene in 25 ml. of acetic anhydride and 1.5 ml. of a 1.54 *M* solution of nitric acid in acetic acid was maintained at 0° for 23 hr. The mixture was hydrolyzed with water and extracted with chloroform. The washed extract was evaporated and the residue was dissolved in the minimum amount of carbon tetrachloride. Chromatography on Bio Rad AG-7 neutral alumina gave a yellow nitro band which was collected in two portions. The eluants were evaporated and homogenized to fine powders which were used to prepare dilute solutions in chloroform for infrared analyses. Intensities at 11.52, 11.71, 11.74, 11.94, 12.07, 12.17, and 12.27 μ were used for the 4-component analyses using averaged extinction coefficients generally of at least two concentrations of standard solutions. Beer's law was obeyed approximately in these analyses. The results are summarized in Table II above. The error is given as the standard deviation.

The nitration in acetic acid was handled in a similar manner: A solution of 1.5 g. of fluoranthene in 30 ml. of acetic acid was allowed to react at 50° for 4.5 hr. with 3 ml. of 0.36 *M* solution of sulfuric acid in acetic acid and 0.3 ml. of concentrated nitric acid. Chromatography and separation into two mixtures was carried out as above. It is interesting to note that an attempt to analyze ultraviolet spectral data of knowns and mixtures with the same computer program as in the infrared analyses gave results with large standard deviations indicating clearly the insufficient differences in ultraviolet spectra of the nitrofluoranthenes for such a multicomponent analysis.

The relative rates of nitration of naphthalene and fluoranthene are summarized in Table III. The indicated amounts of the hydrocarbons were dissolved in 70 ml. of solvent and allowed to react with 0.3 ml. of nitric acid for 28 hr. at 50° in the case of acetic and for 140 hr. at 0° in the case of acetic anhydride. In each run the reaction mixture was diluted with water and extracted with chloroform. The washed and dried extracts were concentrated and aliquots were used directly for gas chromatographic analysis using a 10-ft. silicone rubber on Chromosorb column in a Model 17A F & M gas chromatograph operated at 330°. The peak areas were converted to relative masses by the use of calibration curves. No attempt was made to resolve the nitrofluoranthene peaks. Partial resolution of the nitronaphthalene peaks gave results for α-/β-nitronaphthalene ratio consistent with the independent determinations to follow but not as precise.

Isomer Distribution in Nitration of Naphthalene.—Several experiments were run in which a solution of naphthalene in acetic acid or acetic anhydride was treated with nitric acid. A typical procedure is: To a solution of 3.0 g. of naphthalene in 25 ml. of acetic anhydride maintained at 50.0° in a thermostat was added 1.0 ml. of concentrated nitric acid. After 20 hr. the mixture was diluted with water and extracted with chloroform. The washed and dried extract was concentrated and analyzed directly by gas chromatography as in the previous cases except that a column temperature of 208° was used. The peaks for α- and β-nitronaphthalene were not resolved completely but analysis was possible with the use of extensive calibration curves prepared from known mixtures. The results are summarized in Table IV.

Acknowledgment.—We are indebted to William J. Downs for technical assistance.

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[16] Analysis of Microanalytical Laboratory of the University of California.