concentrated to give a colorless, crystalline residue. This material was sublimed to give 110 mg (18%) of **23**, mp 149–151°. For analysis, a sample was recrystallized from methanol–water.

*Anal.* Calcd for $C_5H_4FN_3$: C, 48.00; H, 3.22; N, 33.59. Found: C, 47.71; H, 3.13; N, 33.75.

**Hydride Reduction of 23.** To a suspension of 150 mg of pulverized lithium aluminum hydride in 15 ml of tetrahydrofuran (purified by distillation from lithium aluminum hydride) was added a solution of 360 mg of **23** in 10 ml of tetrahydrofuran, dropwise with stirring and ice cooling. About 15 min after addition was completed, tlc showed the disappearance of the starting material and the appearance of a small amount of 4-fluorohistamine, together with a new Pauly-positive spot. The mixture was stirred at room temperature for 8 hr; an additional 150 mg of hydride was added and the mixture heated at reflux for 2 hr. Neither treatment effected any visible change (by tlc) in the composition of the reduction mixture. On the basis of tlc, the yield of **22** was judged too small to warrant work-up. Purification and structural studies on the major product of reduction are in progress.

# Homolytic Aromatic Substitution. VIII. Phenylation of Polycyclic Aromatic Hydrocarbons[1,2]

**S. Carlton Dickerman,*[3a] William M. Feigenbaum,[3a] Michael Fryd,[3a] Norman Milstein,[3a] George B. Vermont,[3a] Isaak Zimmerman,[3a,b] and John F. W. McOmie[3c]**

*Contribution from the Department of Chemistry, New York University, University Heights, New York, New York 10453, and the Department of Organic Chemistry, The University, Bristol 8, England.*
*Received September 25, 1972*

**Abstract:** Partial rate factors for homolytic phenylation at all sites in naphthalene, anthracene, biphenylene, and phenanthrene and two of the three positions in pyrene have been measured using the Meerwein reaction and *N*-nitrosoacetanilide as sources. Only phenanthrene exhibited a source effect, and both sets of reactivity data correlate with Hückel localization numbers. The reaction constants determined by the correlations are the lowest ever reported for an aromatic substitution reaction. Other sources were studied with phenanthrene, and 9-acetonylanthracene has been isolated.

The ultimate objective of this research was to test experimentally the correlations of structure and reactivity predicted by theory for homolytic phenylation of polycyclic aromatic hydrocarbons. The general concept, due primarily to Dewar, has been the subject of several reviews.[4–6] Prior to our studies, the molecular affinities of numerous polycyclic arenes for trichloromethyl,[7] methyl,[8a] and trifluoromethyl[8b] radicals had been measured and found to correlate with the lowest localization energy in the particular arene. In none of these studies were the alkylarenes isolated or measured directly. Thus, in making these correlations the total reactivity of every arene must be assigned to only the most reactive positions.[9] Under these circumstances, one is forced to cite the correlation in support of the measurements; nevertheless, the discovery of these relationships had a stimulating effect in this area of physical organic chemistry. In our investigations we have measured partial rate factors for phenylation at 14 sites in five polycyclic aromatic hydrocarbons with two different sources of phenyl radicals, the Meerwein reaction, and *N*-nitrosoacetanilide.

The mechanism of homolytic aromatic substitution, illustrated in eq 1 for the phenyl radical,[10] involves

$$C_6H_5\cdot + ArH \longrightarrow \underset{\mathbf{1}}{C_6H_5ArH\cdot} \longrightarrow C_6H_5Ar \qquad (1)$$

addition to the $\pi$ system giving a cyclohexadienyl type of radical **1** which requires oxidation or dehydrogenation to produce biaryl. Experimental evidence for the formation and existence of the intermediate **1** includes the absence of primary isotope effects[11,12] and the isolation of dimers and disproportionation products of **1**.[13–15] Furthermore, addition of the phenyl radical to benzene has been shown to be irreversible,[16] *vide infra*.

(1) Preliminary reports of parts of these studies have been published: S. C. Dickerman and G. B. Vermont, *J. Amer. Chem. Soc.*, **84**, 4150 (1962); S. C. Dickerman and I. Zimmerman, *ibid.*, **86**, 5048 (1964); S. C. Dickerman, N. Milstein, and J. F. W. McOmie, *ibid.*, 87, 5522 (1965); S. C. Dickerman, *Intra-Sci. Chem. Rep.*, **3**, 247 (1969).

(2) Supported in part by the Aeronautical Research Laboratory, Wright-Patterson Air Force Base, and by an Institutional grant from the American Cancer Society.

(3) (a) New York University; (b) Public Health Predoctoral Fellow of the National Institute of General Medical Studies; (c) The University.

(4) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960, Chapter 2.

(5) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 11.

(6) E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 253 (1964).

(7) E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953).

(8) (a) M. Szwarc, *J. Phys. Chem.*, **61**, 40 (1957); (b) A. P. Stefani and M. Szwarc, *J. Amer. Chem. Soc.*, **84**, 3661 (1962).

(9) For another criticism of methyl affinities, see A. L. J. Beckwith, *J. Chem. Soc.*, 2248 (1962).

(10) The assumption that the phenyl radical is a $\sigma$-type radical has been established by direct examination: P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969), and earlier reports cited therein.

(11) R. I. Milyutinskaya, K. S. Bagdasary, and E. A. Izrealevich, *Russ. J. Phys. Chem.*, **31**, 1019 (1957).

(12) C. C. Price and R. J. Convery, *J. Amer. Chem. Soc.*, **82**, 2938 (1960).

(13) A. F. Bickel and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **71**, 1137 (1952).

(14) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1001 (1957).

(15) D. F. DeTar and R. A. J. Long, *J. Amer. Chem. Soc.*, **80**, 4742 (1958); D. F. DeTar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *ibid.*, **89**, 4051 (1967).

(16) E. L. Eliel, *ibid.*, **82**, 2938 (1960).

**Table I.** Phenylation of Naphthalene and of Naphthalene and Benzene

| Source[a] | Runs[b] | Yield (%) | Recovery[c] (%) | Orientation (%)[d] 1- | 2- | Total rate factor[d] |
|---|---|---|---|---|---|---|
| M | 1, 2 | 1.9 | 87 | 87.5 ± 0.6 | 12.5 ± 0.6 | |
| M | 3, 4 | 1.8 | 92 | 86.6 ± 0.4 | 13.4 ± 0.4 | |
| M | 5–8 | 3.1–3.5 | 91–95 | 86.1 ± 0.6 | 13.9 ± 0.6 | 16.0 ± 0.3 |
| M | (PRF's)[e] | | | 86.6 ± 0.2 | 13.4 ± 0.2 | 16.0 ± 0.3 |
| NAA | 1 | 2.1 | 92 | 84.7 | 15.3 | 16.2 |
| NAA | 2, 3 | 2.3–3.0 | 89–100 | 84.5 ± 0.2 | 15.5 ± 0.2 | 16.4 ± 0.4 |
| NAA | 4 | 3.3 | 92 | 83.4 | 16.6 | 15.2 |
| NAA | (PRF's)[e] | | | 84.3 ± 0.3 | 15.7 ± 0.3 | 16.0 ± 0.3 |

[a] Meerwein (M) and *N*-nitrosoacetanilide (NAA). [b] Number of reactions with multiple analyses of each by glpc. [c] As naphthalene and phenylnaphthalenes. [d] With standard error. [e] Averages used for the calculation of partial rate factors (PRF's) listed in Table VII.

**Table II.** Phenylation of Anthracene and of Anthracene and Benzene

| Source[a] | Runs[b] | Yield (%) | Recovery[c] (%) | Orientation (%)[d] 9- | 1- | 2- | Total rate factor[d] |
|---|---|---|---|---|---|---|---|
| M | 1–6 | | | 84.2 ± 0.3 | 14.0 ± 0.1 | 1.8 ± 0 | |
| M | 7, 8 | 8 | 93–95 | 83.5 ± 0.3 | 13.5 ± 0.3 | (3.0)[e] | 260 ± 3 |
| M | 9, 10 | 8–12 | 90–98 | 85.1 ± 0.1 | 12.0 ± 0.2 | 2.9 ± 0.2 | 272 ± 9 |
| M | 11 | 30 | | 86.6 ± 0.4 | 10.3 ± 0.2 | 3.1 ± 0.4 | |
| M[f] | 12 | 30 | | 85.9 ± 0.8 | 10.9 ± 0.3 | 3.2 ± 0.6 | |
| M | (PRF's)[i] | | | 85.1 ± 0.1 | 12.0 ± 0.2 | 2.9 ± 0.1 | 268 ± 7 |
| NAA | 1–5 | 8–14 | 93–100 | 84.5 ± 0.3 | 11.8 ± 0.1 | 3.7 ± 0.1 | 263 ± 8 |
| NAA[f] | 6, 7 | | | 85.0 ± 0.2 | 11.4 ± 0 | 3.6 ± 0.2 | |
| NAA[g] | 8 | | | 82.9 ± 0.2 | 11.4 ± 0.2 | 5.7 ± 0.3 | |
| NAA[h] | 9 | | | 82.8 ± 0.7 | 11.5 ± 0.2 | 5.6 ± 0.8 | |
| NAA | (PRF's)[i] | | | 84.5 ± 0.3 | 11.8 ± 0.2 | 3.7 ± 0.2 | 263 ± 8 |

[a] Meerwein (M) with *N*-nitrosoacetanilide (NAA). [b] Number of reactions with multiple analyses of each by glpc. [c] As anthracene and phenylanthracenes. [d] With standard error. [e] Estimated. [f] Anthracene-*9,10-d*$_2$. [g] In pyridine. [h] In pyridine plus cupric acetate. [i] Averages used for the calculation of partial rate factors (PRF's) listed in Table VII.

The choice of source of the phenyl radical was dictated by several considerations. First, the phenyl radical must be a primary product of decomposition. This criterion ruled out benzoyl peroxide since it had been demonstrated that anthracene traps the benzoyloxy radical before secondary cleavage.[17] Second, the system should contain an effective oxidizing agent to preclude the formation of dimers and other products from **1**. The Meerwein (M) arylation reaction meets these criteria and was therefore selected as the primary source. The mechanism of this reaction has been extensively investigated and is summarized in eq 1–3.[18]

$$C_6H_5N_2^+ + Cu^{I}Cl_2^- \longrightarrow C_6H_5\cdot + N_2 + Cu^{II}Cl_2 \quad (2)$$

$$C_6H_5ArH\cdot + Cu^{II}Cl^{2-n} \longrightarrow C_6H_5Ar + H^+ + Cu^{I}Cl^{1-n} \quad (3)$$

*N*-Nitrosoacetanilide (NAA) was selected as a second source for general use because it was a proven method of arylation[4] and provided phenyl radicals, directly at a convenient rate at room temperature. The generally accepted mechanism of homolytic phenylation with NAA was established largely by Rüchardt and coworkers[19] and is presented in abbreviated form in eq 1, 3, and 4.[20]

$$C_6H_5N(NO)Ac \longrightarrow C_6H_5N{=}NON{=}NC_6H_5 \longrightarrow C_6H_5\cdot + N_2 + C_6H_5N{=}NO\cdot \quad (4)$$

$$C_6H_5ArH\cdot + C_6H_5N{=}NO\cdot \longrightarrow C_6H_5Ar + C_6H_5N{=}NOH \quad (5)$$

(17) I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 2695 (1952).

(18) For discussion and earlier references, see S. C. Dickerman, D. J. DeSouza, and N. Jacobson, *J. Org. Chem.*, **34**, 710 (1969).

(19) C. Rüchardt and B. Freudenberg, *Tetrahedron Lett.*, 3623 (1964); G. Binsch and C. Rüchardt, *J. Amer. Chem. Soc.*, **88**, 173 (1966); G. Binsch, E. Merz, and C. Rüchardt, *Chem. Ber.*, **100**, 247 (1967).

(20) There has been some uncertainty as to whether $C_6H_5N{=}NO\cdot$ is the radical primarily responsible for dehydrogenation of **1**; for details, see J. I. G. Cadogan, R. M. Paton, and C. Thomson, *Chem. Commun.*, 614 (1969), and earlier references cited therein.

## Results and Discussion

All of the data reported here were obtained using glpc for analysis. Authentic samples of all monophenyl derivatives were in hand, and blank reactions, in which the arene was absent, were run to determine whether any by-products of reaction would interfere with the desired analysis. Identification of the peaks in the chromatogram was accomplished by addition of authentic phenylarene to an aliquot of the reaction mixture and in part by identification of "peaks" collected from the gas chromatograph. Conversions were kept low, and two amounts of internal standard were employed: a small amount for the phenylarenes and a much larger amount for quantitative determination of unreacted arene. Total rate factors were calculated by eq 6 in which

$$k_{arene}/k_{benzene} = [\text{phenylarenes}][\text{benzene}]_0/[\text{biphenyl}][\text{arene}]_{TA} \quad (6)$$

the initial concentration of arene has been replaced by the time-averaged value.[21] The results are reported in Tables I–VI with corresponding details with respect to reagents, etc., in Table IX in the Experimental Section.

The data obtained for M and NAA phenylations of naphthalene are given in Table I. Both the M reaction, in aqueous acetone at room temperature, and NAA, in benzene also at room temperature, yield similar results. A somewhat smaller total rate factor and less 1-phenylnaphthalene were measured earlier for NAA phenyla-

(21) Use of an integrated or half-integrated formula is superfluous in view of the fact that some benzene is produced in both arylation systems, particularly the M reaction.

Table III. Phenylation of Anthracene (A) and Naphthalene (N)

| Source[a] | Runs[b] | Yield (%) A | Yield (%) N | Recovery[c] (%) A | Recovery[c] (%) N | Orientation (%)[d] 9- | Orientation (%)[d] 1- | Orientation (%)[d] 2- | Reactivity[d] A/N |
|---|---|---|---|---|---|---|---|---|---|
| M | 1–4 | 32–34 | 2.8–2.9 | 78–84 | 92–96 | 86.1 ± 0.2 | 13.9 ± 0.2<br>85.3 ± 0.3 | 14.7 ± 0.3 | 16.2 ± 0.5 |

[a] Meerwein (M). [b] Number of reactions with multiple analyses of each by glpc. [c] As anthracene and phenylnaphthalenes. [d] With standard error.

Table IV. Phenylation of Biphenylene and Benzene

| Source[a] | Runs[b] | Yield (%) | Recovery[c] (%) | Orientation (%)[d] 1- | Orientation (%)[d] 2- | Total rate factor[d] |
|---|---|---|---|---|---|---|
| M | 1–6 | 2.7–3.2 | 91–101 | 24.8 ± 0.3 | 75.2 ± 0.3 | 19.0 ± 0.5 |
| NAA | 1–6 | 5.7–7.4 | 86–97 | 22.6 ± 0.3 | 77.4 ± 0.3 | 20.0 ± 0.3[e] |

[a] Meerwein (M) and *N*-nitrosoacetanilide (NAA). [b] Number of reactions with multiple analyses of each by glpc. [c] As biphenylene and phenylbiphenylenes. Meerwein reactions corrected for an 8% loss of biphenylene during work-up. [d] With standard error. [e] In air the total rate factor has a value of only about 13.

Table V. Phenylation of Pyrene and Benzene

| Source[a] | Runs[b] | Yield (%) | Recovery[c] (%) | Orientation (%)[d,e] 1- | Orientation (%)[d,e] 4- | Total rate factor[d] |
|---|---|---|---|---|---|---|
| M | 1–4 | 5.4–6.7 | 96–99 | 73.5 ± 0.9 | 26.5 ± 0.9 | 78.5 ± 0.8 |
| NAA | 1–5[f] | 6.0–7.1 | 96–100 | 70.0 ± 0.0 | 30.0 ± 0.0 | 81.4 ± 0.4 |

[a] Meerwein (M) and *N*-nitrosoacetanilide (NAA). [b] Number of reactions with multiple analyses of each for TRF by glpc. [c] As pyrene and phenylpyrene. Meerwein reactions corrected for 3% loss of pyrene during work-up. [d] With standard error. [e] With Du Pont 310 curve resolver and standard mixtures. [f] Three determinations of orientation.

Table VI. Phenylation of Phenanthrene and of Phenanthrene and Benzene

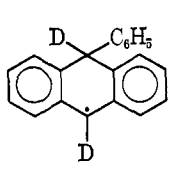
| Source[a] | Runs[b] | Solvent[c] | Temp, °C | Orientation (%)[d] 9- + 1- | 4- | 3- | (or +) | 2- | Total rate factor[d] |
|---|---|---|---|---|---|---|---|---|---|
| M | 1, 2 | A, W | 30 | 58.1 ± 0.2 | 30.3 ± 0.2 | | 11.6 ± 0.4 | | 17.6 ± 0.2[e] |
| M | 3, 4 | A, W | 30 | 54.7 ± 0.4 | 32.7 ± 0.4 | 8.0 ± 0.3 | | 4.6 ± 0.3 | |
| M | 5, 6 | A, W | 30 | 54.4 ± 0.3 | 33.2 ± 0.2 | 7.6 ± 0.1 | | 4.8 ± 0.1 | |
| M | 7, 8[g] | A, W | 30 | 56.2 ± 0.2 | 30.6 ± 0.1 | 7.4 ± 0.1 | | 5.8 ± 0.0 | |
| M | 9, 10 | A, W | 30 | 56.8 ± 0.1 | 30.9 ± 0.1 | | 12.3 ± 0.1 | | |
| M | (PRF's)[l] | A, W | 30 | 58.1 ± 0.2 | 30.3 ± 0.2 | 7.0 ± 0.4 | | 4.6 ± 0.4 | 17.6 ± 0.2 |
| M | 11, 12 | A, W | 4 | 52.5 ± 0.1 | 34.6 ± 0.3 | 7.7 ± 0.1 | | 5.2 ± 0.1 | |
| M | 13, 14 | A, W | 60 | 58.5 ± 0.5 | 27.2 ± 0.4 | 7.4 ± 0.3 | | 6.9 ± 0.4 | |
| NAA | 1, 2 | B | 30 | 56.2 ± 0.6 | 19.5 ± 0.2 | | 24.3 ± 0.8 | | 18.1 ± 0.4[f] |
| NAA | 3, 4 | B | 30 | 54.6 ± 0.2 | 23.0 ± 0.1 | 11.8 ± 0.1 | | 10.6 ± 0.2 | |
| NAA | (PRF's)[l] | B | 30 | 55.4 ± 0.5 | 21.2 ± 1 | 12.3 ± 0.4 | | 11.1 ± 0.4 | 18.1 ± 0.4 |
| NAA | 5, 6 | B | 4 | 57.2 ± 0.7 | 19.2 ± 0.6 | 12.8 ± 0.4 | | 10.7 ± 0.6 | |
| NAA | 7, 8 | B | 60 | 55.9 ± 0.3 | 24.6 ± 0.2 | 11.4 ± 0.4 | | 8.1 ± 0.3 | |
| NAA | 9, 10 | A, W | 30 | 55.7 ± 0.2 | 24.4 ± 0.3 | 11.4 ± 0.2 | | 8.5 ± 0.3 | |
| NAA | 11, 12[h] | BB | 30 | 60.6 ± 0.4 | 20.3 ± 0.3 | 11.5 ± 0.6 | | 7.6 ± 0.3 | |
| NAA | 13, 14 | B[i] | 30 | 60.5 ± 0.5 | 16.6 ± 0.4 | 12.8 ± 0.2 | | 10.1 ± 0.3 | |
| DAB | 1, 2 | None | 152 | 43.8 ± 0.3 | 28.4 ± 0.2 | 15.9 ± 0.1 | | 11.9 ± 0.3 | |
| DAB | 3, 4 | BB | 156 | 52.1 ± 0.6 | 23.0 ± 0.1 | 14.5 ± 0.1 | | 10.4 ± 0.2 | |
| BP | 1, 2[j] | B | 80 | 54.0 ± 0.2 | 25.2 ± 0.2 | 11.7 ± 0.3 | | 9.1 ± 0.2 | |
| BP | 3, 4[j] | B[k] | 80 | 59.6 ± 0.5 | 24.5 ± 0.1 | 9.5 ± 0.3 | | 6.5 ± 0.1 | |
| WW | 1, 2 | A | 30–40 | 60.1 ± 0.5 | 20.4 ± 0.2 | 13.2 ± 0.5 | | 6.3 ± 0.1 | |

[a] M (Meerwein), NAA (*N*-nitrosoacetanilide), DAB (diazoaminobenzene), BP (benzoyl peroxide), WW (Waters). [b] Number of reactions with multiple analyses of each by glpc. [c] A (acetone), W (water), B (benzene), BB (bromobenzene). [d] With standard error. [e] Yields of 2.2–2.6% and recoveries of 95–100% as phenanthrene and phenylphenanthrenes. [f] Yields of 3.7–4.7% and recoveries of 95–101% as phenanthrene and phenylphenanthrenes. [g] Before column chromatography 51% 9 and 1, 34% 4, 9% 3, and 6% 2 isomer. [h] Not column chromatographed. [i] With oxygen bubbled through reaction mixture. [j] Hydrolyzed with alcoholic KOH before column chromatography. [k] Under oxygen. [l] Averages used for calculation of partial rate factors (PRF's) listed in Table VII.

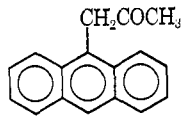
tion using a different method of analysis.[22] Other sources have been employed at higher temperatures.[23]

The results of M and NAA phenylations of anthracene are reported in Table II. Again the two different sources gave similar data. Anthracene-*9,10-d*$_2$ was also phenylated, runs M 18 and NAA 6,7, to determine whether isotopic substitution at these positions would lead to formation of less 9-phenylanthracene and more of the 1 and 2 isomers. Such a result would be expected if formation of radical **2** were reversible or if dimerization and disproportionation of radicals like **2** were occurring to a significant extent in M and NAA phenylations of anthracene. However, isotopic substitution failed to produce an observable effect on orientation.

(22) R. Huisgen, F. Jacob, and R. Grashey, *Chem. Ber.*, **92**, 2206 (1959).
(23) D. I. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3112 (1961).




2




3

Substitution of pyridine for benzene in NAA phenylation did shift the orientation from the 9 to the 2 isomer which suggests some change in mechanism. In addition to the results reported in Table II, acetone was used as the solvent for NAA phenylation of anthracene. Examination by glpc revealed an unusually complicated reaction mixture. A major component of this chromatogram was isolated from a preparative reaction and was found to be 9-acetonylanthracene (3). Presumably this compound is produced by homolytic acetonylation of anthracene. Chain transfer with solvent molecules, acetone, is the obvious source of the acetonyl radicals, eq 7.[24] The same chain transfer reaction also occurs in the M reaction but here the acetonyl radical is converted efficiently to chloroacetone by redox-ligand transfer, eq 8. Evidence that homolytic acetonylation is at best a minor side reaction in M phenylation is the fact that orientation and total rate factors for this reaction and for NAA, in benzene where the acetonyl radical is not a factor, are virtually identical not only for anthracene but for all of the other arenes except phenanthrene.

$$C_6H_5\cdot \text{ and/or } R\cdot + CH_3COCH_3 \longrightarrow C_6H_5 \text{ and/or } RH + CH_3COCH_2\cdot \quad (7)$$

$$Cu^{II}Cl_n^{2-n} + CH_3COCH_2\cdot \longrightarrow CH_3COCH_2Cl + Cu^{I}Cl_{n-1}^{2-n} \quad (8)$$

The results of a competitive phenylation of anthracene *vs.* naphthalene under M reaction conditions are reported in Table III. These experiments provide a check of the total rate factors obtained in competition with benzene. Thus, a reactivity ratio of 16.2 for anthracene relative to naphthalene, multiplied by the total rate factor of 16.0 for naphthalene from Table I, gives a total rate factor for anthracene of 259. As reported in Table II, direct competition gave values of 260–272.

Biphenylene was the next arene selected for study and the results are given in Table IV. These findings have particular significance with respect to theory since predictions of the more reactive position in this arene based on free valence and localization indices are directly opposed.[5] Examination of the data in Table IV reveals that the 2 position is indeed the more reactive in homolytic aromatic substitution agreement with the lower localization index for that position.

At this point in these studies enough information had been accumulated to permit predictions of partial rate factors, and thus orientation, for other arenes by means of a correlation of the type shown in the next section. In particular it was possible to predict that homolytic phenylation of pyrene should furnish about 70% 1-, 30% 4-, and less than 1% 2-phenylpyrene.[25] The results of M and NAA phenylations of pyrene are recorded in Table V and demonstrate the predictive success of the correlation. Collection of the single peak corresponding in retention time to 1- and 4-phenylpyrene and examination of the sample by infrared showed the presence of both isomers. Subsequent use of a more polar column gave partial resolution and thus quantitative analysis.

Homolytic phenylation of phenanthrene was also studied with several sources and under a variety of conditions as shown in Table VI.[26] This arene presented special problems. For example, phenanthrene has five different reaction sites and although the 9 and 1 isomers were not separated, it was difficult to place the remaining four peaks in "free" regions of the chromatograms. Furthermore, the ratio of source to phenanthrene had to be increased, relative to those used for the other arenes (compare naphthalene with about the same total rate factor and phenanthrene in Table IX) in order to produce measurable amounts of 3- and particularly 2-phenylphenanthrene. This procedure increased the amount of by-products and thus created additional problems. In particular, infrared examination of the collected peak corresponding in retention time to 9- and 1-phenylphenanthrene, produced in the M reaction, revealed not only the presence of both isomers but also some absorption in the carbonyl region.[27] Presumably this absorption indicates the presence of acetonyl derivatives formed in the manner discussed above in connection with the phenylation of anthracene. The magnitude of the analytical problem posed by the presence of these by-products was estimated by comparison of isomer distribution before and after column chromatography, M 7,8 in Table VI, under conditions which produced collected samples free of carbonyl absorption. Although this procedure revealed only faily small differences, column chromatography of samples prior to analysis by glpc was adopted as a general procedure in these studies of phenanthrene. Another reason was the knowledge that use of additional sources, *e.g.*, benzoyl peroxide and diazoaminobenzene, would necessitate this procedure in any event.

Comparison of the results of M and NAA phenylations of phenanthrene reveal significant differences in orientation in contrast to the other arenes studied. The M reaction yields half-again as much 4-phenylphenanthrene and correspondingly smaller amounts of the 3 and 2 isomers. Phenylations with diazoaminobenzene (DAB) and benzoyl peroxide (BP), both at higher reaction temperatures, gave orientation data intermediate between those for the M and NAA reactions.[28] The Waters reaction (WW), in which phenyl radicals are produced by zinc dust reduction of benzenediazonium tetrachlorozincate, furnished another set of orientation values.[29] As anticipated, both the WW re-

(24) The occurrence of this side reaction in NAA phenylations in acetone–water and the insolubility of benzenediazonium chloride in benzene precluded a general comparison of NAA and M phenylations of arenes in the same solvent. However, see Table VI.

(25) In contrast to the results of a previous study that had revealed formation of only 1-phenylpyrene: R. O. C. Norman, G. A. Thompson, and W. A. Waters, *J. Chem. Soc.*, 179 (1958).

(26) Choronologically, phenanthrene was investigated early in this study and is treated last for clarity of presentation.

(27) In contrast, M phenylation of anthracene, biphenylene, and pyrene produced samples of phenylarenes from the chromatograph which were free of carbonyl absorption in the infrared.

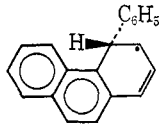
(28) Diazoaminobenzene and benzoyl peroxide were included in this study because it had been reported that phenylation of phenanthrene with these sources produced all of the isomers except 4-phenylphenanthrene [A. L. J. Beckwith and M. J. Thompson, *J. Chem. Soc.*, 73 (1961)]. After preliminary publication of our results,[1] Professor Beckwith privately communicated the information that another analysis of their reaction mixtures had revealed the presence of 4-phenylphenanthrene.

(29) This reaction was developed and used principally by W. A. Waters and coworkers; *e.g.*, see R. O. C. Norman and W. A. Waters, *J. Chem. Soc.*, 167 (1958); and P. S. Johnson and W. A. Waters, *ibid.*, 4652 (1962).

action in the usual solvent, acetone, and NAA in aqueous acetone, NAA 9,10 in Table VI, furnished a complex mixture of products before column chromatography.

The common feature of all of these sources is formation of phenyl radicals. However, it is unlikely that this highly reactive radical can be responsible for dehydrogenation of significant amounts of the intermediate radical **1** formed by addition to phenanthrene. Thus, in comparing these sources we are in effect comparing different oxidizing or dehydrogenating agents. In the M and NAA reactions it is a form of cupric ion and $C_6H_5N{=}NO\cdot$ (or similar radical), respectively, *vide supra*. For BP phenylations it is the peroxide itself in an induced decomposition and the benzoyloxy radical.[15,30,31] In the DAB and WW reactions it is presumably the anilino radical ($C_6H_5NH\cdot$) and the acetonyl radical, respectively. If the dehydrogenation step is less than 100% efficient, the intermediate radical **1** is presented with an opportunity to dimerize and disproportionate. Addition of the phenyl radical to phenanthrene produces five different radicals for possible participation in both dimerization and disproportionation. If the occurrence of these side reactions alters the composition of product, in this instance the phenylphenanthrenes, they have been termed selective, otherwise, nonselective.[30] Since there is no *a priori* method of determining the "true" composition of the isomeric phenylarenes, any type of arylation reaction must be evaluated by comparison with other sources or by perturbation of reaction conditions.[32] Thus, the source effect detected in the phenylation of phenanthrene is indicative of the occurrence of selective side reactions in all but one of the arylation reactions studied.

Examination of the data for Meerwein phenylation of phenanthrene in Table VI reveals that this reaction consistently yields more 4 than 9 or, more probably, 1 isomer in spite of the fact that the localization indices predict the order 9- > 1- > 4-.[5] Since phenanthrene has been shown to deviate slightly from planarity in the crystalline state,[33] it is reasonable to invoke the concept of steric acceleration to account for the observed rate enhancement at the 4,5 positions in this arene.[34] However, the product of addition at these positions, radical **4**, must exhibit steric hindrance to oxidation or dehydrogenation in comparison to the isomers that are formed by addition at the remaining sites. Thus, the increased amounts of 4-phenylphenanthrene produced in the M reaction, relative to the other sources, are attributed to the ability of cupric ion to aromatize **4**. Furthermore, the occurrence of selective side reactions in arylations of phenanthrene may be rationalized by the presence of radical **4**, which is unique to this substrate.[35]




**4**

Several additional experiments require comment. The phenylation of phenanthrene with benzoyl peroxide under oxygen rather than nitrogen (BP 3,4 in Table VI) was designed by analogy with the work described in ref 32. These in turn were based upon the earlier observation that molecular oxygen would oxidize intermediate **1** to biaryl and that it would do so in preference to the unusual pathway, reaction with peroxide itself.[36] Again phenanthrene exhibited a "source effect" in that the reaction under oxygen gave more 9 and 1 isomers, and less 3- and 2-phenylphenanthrenes, than that under nitrogen. Similar experiments with NAA, compare NAA 3,4 and NAA 13,14, resulted in less 4 isomer and more 9- and 1-phenylphenanthrenes. An attempt was made to assay the effect of reaction temperature on orientation in M and NAA phenylations of phenanthrene with mixed results. Comparison of reactions designated M 11,12, M 7,8, and M 13,14 in Table VI reveals that a change in reaction temperature from 4 to 30 to 60° resulted primarily in a decrease in the relative amount of 4 isomer. In similar experiments with NAA an opposite effect was observed, compare NAA 5,6, NAA 3,4, and NAA 7,8 in Table VI. However, in experiments of this type, it is impossible, at least at this time, to isolate the effects produced solely by changes in reaction temperature from those caused by alterations in mechanism.[37]

**Partial Rate Factors and Correlations.** Partial rate factors for homolytic phenylation at 14 positions in the five arenes included in this investigation have been calculated from the orientation and total rate data given in Tables I–VI for both the Meerwein and *N*-nitrosoacetanilide reactions. These two sets of partial rate factors ($F_n$) are listed in Table VII. Although there is now considerable latitude with respect to the choice of calculated reactivity index,[38] the one most often employed in correlating partial rate factors for aromatic substitution has been Hückel localization numbers. Therefore to facilitate comparisons, the logarithms of the partial rate factors are plotted in Figures 1 and 2 against the difference in Hückel localization numbers between positions n in the arene ($L_n$) and that for benzene ($L_o$).[39] The form of the relationships demonstrated in Figures 1 and 2 is given by eq 9 in

$$\log F_n = (L_n - L_o)\beta/2.3RT \qquad (9)$$

which the variable on the right-hand side of the equation ($\beta$) has the connotation of a reaction constant.[4-6] As

(30) For a review of aromatic arylation with particular emphasis on the peroxide reaction, see D. H. Hey, *Advan. Free-Radical Chem.*, **2**, 47 (1967).

(31) For a computer analysis of the importance of the many steps in benzoyl peroxide decompositions in benzene, see D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967).

(32) The latter method has been used to demonstrate that the side reactions in peroxide arylations of several substituted benzenes are essentially nonselective: R. T. Morrison, J. Cazes, N. Samkoff, and C. A. House, *ibid.*, **84**, 4152 (1962).

(33) J. Trotter, *Acta Crystallogr.*, **16**, 605 (1963).

(34) This concept had been proposed earlier to account for enhanced rates of deuteriodeprotonation from the 4,5 positions in phenanthrene, and similar sites in other arenes: G. Dallinga, E. L. Mackor, and A. A. Verrign Stuart, *Mol. Phys.*, **1**, 123 (1958); G. Dallinga, P. J. Smit, and E. L. Mackor in "Steric Effects in Conjugated Systems," G. W. Gray, Ed., Buttersworths, London, 1958, Chapter 13.

(35) The remarkable feature of this study of phenanthrene is not the detection of a source effect but rather that such diverse sources yield all five phenylphenanthrenes in not too dissimilar amounts.

(36) M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, **27**, 2289 (1962).

(37) In fact, 1,4-dihydrobiphenyl, a product diagnostic of side reactions, was isolated from a decomposition of NAA in benzene at 60°. This compound could not be detected by glpc in a duplicate reaction at 30°.

(38) For example, see M. J. S. Dewar and C. C. Thompson, Jr., *J. Amer. Chem. Soc.*, **87**, 4414 (1965).

(39) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of $\pi$-Electron Calculations," W. H. Freeman, San Francisco, Calif., 1965.

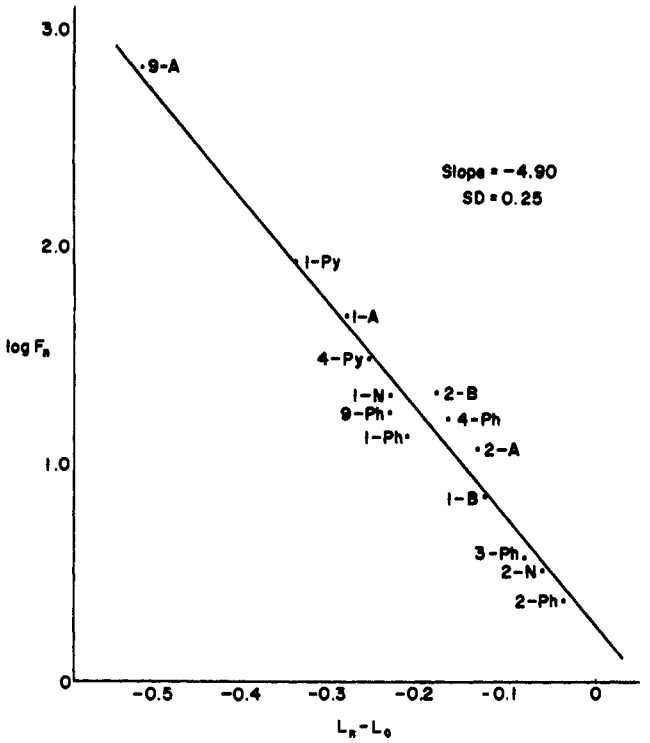



Figure 1. Plot of partial rate factors for Meerwein phenylation of polycyclic aromatic hydrocarbons *vs.* differences in Hückel localization numbers: A (anthracene), N (naphthalene), B (biphenylene), Py (pyrene), Ph (phenanthrene).

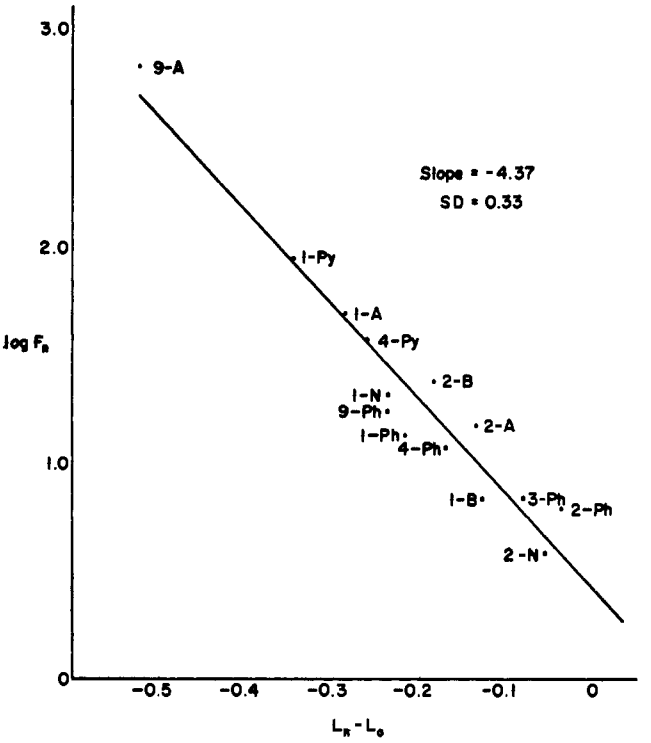



Figure 2. Plot of partial rate factors for *N*-nitrosoacetanilide phenylation of polycyclic aromatic hydrocarbons *vs.* differences in Hückel localization numbers: A (anthracene), N (naphthalene), B (biphenylene), Py (pyrene), Ph (phenanthrene).

**Table VII.** Partial Rate Factors of Polycyclic Aromatic Hydrocarbons in Homolytic Phenylation at 30°

| Arene | Position | Partial rate factor ($F_n$) Meerwein | Partial rate factor ($F_n$) *N*-Nitrosoacetanilide |
|---|---|---|---|
| Naphthalene | 1 | 20.8 | 20.2 |
| | 2 | 3.22 | 3.77 |
| Anthracene | 9 | 684 | 667 |
| | 1 | 48.2 | 46.5 |
| | 2 | 11.7 | 14.6 |
| Biphenylene | 1 | 7.07 | 6.78 |
| | 2 | 21.4 | 23.2 |
| Pyrene | 1 | 86.5 | 85.5 |
| | 4 | 31.2 | 36.6 |
| Phenanthrene | 9 | 17.2[a] | 16.8[a] |
| | 1 | 13.5[a] | 13.2[a] |
| | 4 | 16.0 | 11.5 |
| | 3 | 3.70 | 6.68 |
| | 2 | 2.43 | 6.03 |

[a] Assuming that the combined amounts of 9- and 1-phenylphenanthrene from Table VI are divided 56% 9 and 44% 1 isomer, see text.

indicated previously, the mixture of 9- and 1-phenylphenanthrenes could not be separated. However, partial rate factors for these positions have been estimated from the total rate factor, the combined percentage, and the ($L_n - L_o$) numbers for these two positions; that is, by dividing eq 9 for the 9 position in phenanthrene by the corresponding equation for the 1 position in this arene, substitution and solution. Although this procedure assumes in part the desired correlation, it is preferable to the alternative of either using none or only part of the data for phenanthrene. In particular, enhanced reactivity at the 4,5 positions in phenanthrene in the M reaction must be accompanied by a decrease in one or more of the other isomers and exclusion of the partial rate factors for the 9 and 1 positions, which account for more than half of the reactivity, would prejudice any correlation. Therefore, partial rate factors for the 9 and 1 positions in phenanthrene have been included in Table VII and in Figures 1 and 2.

The slopes given in Figures 1 and 2 were determined by the method of least squares and, in conjunction with eq 9, were used to calculate the reaction constant ($\beta$). Thus, homolytic phenylation of arenes using the Meerwein reaction and *N*-nitrosoacetanilide as sources was found to exhibit reaction constants of $-6.77$ and $-6.03$ kcal/mol, respectively.[40] A comparison of these $\beta$ values with those reported for other aromatic substitution reactions, as shown in Table VIII, reveals that homolytic phenylation exhibits the smallest reaction

**Table VIII.** Substitution of Polycyclic Aromatic Hydrocarbons

| Reaction | Reaction constant $\beta$, kcal/mol[a] |
|---|---|
| Phenylation | $-6.8$ ($-6.0$) |
| Methylation[b] | $-11$ |
| Trichloromethylation[b] | $-20$ |
| Nitration[c] | $-9.4$ |
| Chlorination[c] | $-29$ |
| Bromination[d] | $-31$ |

[a] *Versus* Hückel localization numbers. [b] From ref 5, Chapter 13. [c] Reaction constants *vs.* Dewar reactivity numbers from ref 6, multiplied by a factor of 2, see ref 41. [d] From ref 42.

(40) Use of dimensionless Hückel localization numbers, rather than energies as recommended by Streitwieser,[6] means that $\beta$ has the units of cal or kcal/mol.

Table IX. Reagents, Etc., in Homolytic Phenylation[a]

| Code[b] | Reactants (mmol) Arene | Benzene | Aniline | $CuCl_2 \cdot 2H_2O$ | Other[d] source | Solvent,[c] ml | Temp, °C |
|---|---|---|---|---|---|---|---|
| | | | Naphthalene | | | | |
| M 1, 2 | 4.00 | | 6.00 | 2.00 | | 200 A, 50 W | 30 |
| M 3, 4 | 4.00 | | 6.00 | 4.00 | | 200 A, 50 W | 30 |
| M 5–8 | 10.0 | 200 | 6.00 | 5.00 | | 200 A, 50 W | 30 |
| NAA 1 | 50 | 800 | | | 6.1 | | 30 |
| NAA 2, 3 | 50 | 800 | | | 12 | | 30 |
| NAA 4 | 50 | 800 | | | 18 | | 30 |
| | | | Anthracene | | | | |
| M 1–6 | 2.00 | | 12.0 | 2.00 | | 400 A, 100 W | 30 |
| M 7, 8 | 4.00 | 1000 | 12.0 | 2.00 | | 450 A, 110 W | 30 |
| M 9, 10 | 0.123 | 22.4 | 0.275 | 0.090 | | 22.4 A, 5.6 W | 30 |
| M 11 | 0.115 | 22.4 | 0.550 | 0.177 | | 22.4 A, 5.6 W | 30 |
| M 12 | 0.115 | 22.4 | 0.550 | 0.177 | | 22.4 A, 5.6 W | 30 |
| NAA 1–5 | 8.00 | 2000 | | | 4.3 | | 30 |
| NAA 6, 7 | 0.14 | 33.6 | | 0.08 | | | 30 |
| NAA 8 | 8.00 | | | 4.0 | | 20 P | 30 |
| NAA 9 | 8.00 | | 4.00[e] | | | 20 P | 30 |
| | | | Anthracene and Naphthalene | | | | |
| M 1–4 | 0.628 A<br>10.0 N | | 12.0 | 5.00 | | 200 A, 50 W | |
| | | | Biphenylene | | | | |
| M 1–6 | 0.170 | | 11.2 | 0.55 | 0.181 | 11.2 A, 2.8 W | 30 |
| NAA 1–6 | 0.182 | | 11.2 | | 0.16 | | 30 |
| | | | Pyrene | | | | |
| M 1–4 | 0.500 | | 34.0 | 1.35 | 0.750 | 30.0 A, 4.8 W | 30 |
| NAA 1–5 | 3.00 | | 240 | | 1.5 | | |
| | | | Phenanthrene | | | | |
| M 1, 2 | 6.51 | 555 | 26.0 | 2.17 | | 270 A, 67 W | 30 |
| M 3, 4 | 3.26 | 55.5 | 26.0 | 1.08 | | 270 A, 67 W | 30 |
| M 5, 6 | 6.51 | 111 | 26.0 | 1.08 | | 270 A, 67 W | 30 |
| M 7, 8 | 6.51 | 111 | 26.0 | 2.17 | | 270 A, 67 W | 30 |
| M 9, 10 | 6.51 | 111 | 26.0 | 4.34 | | 270 A, 67 W | |
| M 11, 12 | 6.51 | 111 | 26.0 | 4.34 | | 270 A, 67 W | 4 |
| M 13, 14 | 6.51 | 111 | 26.0 | 4.34 | | 270 A, 67 W | 60 |
| NAA 1, 2 | 6.51 | 111 | | | 3.0 | | 30 |
| NAA 3, 4 | 6.51 | 111 | | | 3.0 | | 30 |
| NAA 5, 6 | 6.51 | 111 | | | 3.0 | | 4 |
| NAA 7, 8 | 6.51 | 111 | | | 3.0 | | 60 |
| NAA 9, 10 | 0.651 | 11.1 | | | 2.6 | 27 A, 7 W | 30 |
| NAA 11, 12 | 5.50 | | | | 2.5 | 10 BB | 30 |
| NAA 13, 14[f] | 6.51 | 111 | | | 3.0 | | 30 |
| DAB 1, 2 | 5.60 | | | | 0.80 | None | 152 |
| DAB 3, 4 | | | | | 6.6 | 11.2 BB | 156 |
| BP 1, 2 | 6.51 | 111 | | | 3.00 | | 80 |
| BP 3, 4[g] | 6.51 | 111 | | | 3.25 | | 80 |
| WW 1, 2 | 0.651 | 11.1 | | | 3.0 | 35 A | 30–40 |

[a] Under nitrogen unless otherwise specified. [b] M (Meerwein), NAA (*N*-nitrosoacetanilide), DAB (diazoaminobenzene), BP (benzoyl peroxide), WW (Waters). [c] A (acetone), W (water), BB (bromobenzene), P (pyridine). [d] See code for identification. [e] Cupric acetate. [f] With oxygen bubbled through reaction mixture. [g] Under oxygen.

constant.[41] The magnitude of $\beta$ reflects the position of the transition state along the reaction coordinate or the approach to a transition state that is identical with the Wheland intermediate. Thus, the transition state for homolytic phenylation appears earliest along the reaction coordinate and deviates the most from the Wheland intermediate. Synonymously, the phenyl radical must be the most reactive species among those affecting aromatic substitution. A high degree of reactivity is associated with a lack of selectivity and this is why homolytic phenylation of naphthalene, anthracene, biphenylene, pyrene, and phenanthrene yields measurable amounts of all positional isomers with but a single exception, 2-phenylpyrene. By way of contrast, only a single isomer has been detected in the bromination of naphthalene, anthracene, pyrene, and phenanthrene[42] and in the nitration of pyrene.[43]

## Experimental Section

**Reagents.** Eastman or standard grades of Aldrich naphthalene, anthracene, phenanthrene, and pyrene were purchased. Bi-

(41) There may be a residue of confusion on this point because of earlier correlations with Dewar localization numbers rather than Hückel localization numbers. Since the former have just about half the magnitude of the latter, reaction constants determined with these parameters will be correspondingly smaller.

(42) L. Altschueler and E. Berliner, *J. Amer. Chem. Soc.*, 88, 5837 (1966).

(43) Only 1-nitropyrene was detected in this study by P. M. C. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, 164 (1956). Since the three isomeric nitropyrenes were in hand, as precursors in the synthesis of the corresponding phenylpyrenes, the nitration of pyrene was reinvestigated with a variety of sources including nitronium tetrafluoroborate. However, 4-nitropyrene was not produced in amounts detectable by glpc in any of these reaction: unpublished results of W. M. Feigenbaum.

phenylene was synthesized in the laboratory of Professor J. F. W. McOmie. 9-Phenylanthracene and 1- and 2-phenylnaphthalene were obtained from the Aldrich Chemical Co., Inc. The remaining isomeric phenylanthracenes, all five isomeric phenylphenanthrenes,[44] and the three phenylpyrenes[45] have been described in the literature. Both 1- and 2-phenylbiphenylene were synthesized expressly for these studies.[46] All samples of the hydrocarbons were tested for homogeneity by glpc and purified as required by column chromatography on alumina. Anthracene-*9,10-d*$_2$, prepared from 9,10-dilithioanthracene[47] and deuterium oxide, exhibited a melting point of 215–218° (lit.[46] mp 216–218°), after crystallization from 95% ethanol. The virtual absence of absorption at 885 cm$^{-1}$ in the infrared indicated a minimum of 90% isotopic substitution at the 9,10 positions. The other organic and inorganic chemicals used were reagent grade.

**Typical Procedures.** The amounts of reagents and solvents corresponding to each entry in Tables I–VI are listed in Table IX.

For the M reactions, aniline was treated with 3 equiv of 6 *F* hydrochloric acid and diazotized with 1 equiv of sodium nitrite. This solution was added dropwise under nitrogen to a solution of arene, acetone, water, benzene, and cupric chloride dihydrate at room temperature. After standing overnight or for several hours, the reaction mixture was diluted with excess water and then extracted with several portions of methylene chloride or benzene. The combined extracts were washed with 5% sodium hydroxide and water and dried over anhydrous magnesium sulfate. After filtration, almost all of the solvent was removed under reduced pressure. Internal standards were added at this point and the mixture was dissolved in the minimum volume of benzene or, in the case of phenanthrene, the residue was dissolved in benzene and chromotographed on Florisil using cyclohexane as eluent and fluorescence under ultraviolet light as the monitor. After removal of the cyclohexane, the residue was dissolved in benzene and analyzed.

*N*-Nitrosoacetanilide, prepared in the usual manner,[49] was precipitated from water and washed by decantation with additional ice–water. After filtration, the yellow solid was dried by spreading on paper towels and pressing gently with a spatula until the material was powdered, mp 51–52° dec (lit.[49] mp 50–51° dec). If stored slightly wet at −20°, samples maintained their melting point and color for several weeks. In these phenylations the reaction mixtures were allowed to stand overnight at room temperature and then analyzed neat after removal of part of the solvent. With phenanthrene, column chromatography on neutral alumina (Woelm I) preceded analysis.

Diazoaminobenzene, prepared in the usual manner,[28] was used to phenylate phenanthrene as outlined in Table IX. The reaction mixtures were chromatographed on neutral alumina (Woelm I) with benzene as the eluent before analysis.

The benzoyl peroxide phenylations of phenanthrene were accomplished by heating the reaction mixtures at 80° for 36 hr. At that point a 20% solution of potassium hydroxide in ethanol was added and the reaction mixture was refluxed for an additional 12 hr. This solution was poured into water and additional benzene was added. The organic layer was separated and the water layer extracted with additional benzene. The combined extracts were washed with water until neutral and then dried with magnesium sulfate. After filtration of the drying agent, the solvent was removed and the residue was chromatographed on neutral alumina (Woelm I) with hexane–benzene (3:1). The combined and concentrated eluent was then analyzed.

Phenylation of phenanthrene with the Waters reaction was accomplished by adding zinc powder in small portions to a well-stirred mixture of arene, benzene, acetone, and benzenediazonium tetrachlorozincate under nitrogen.[39] After addition of all of the zinc powder, the mixture was stirred at room temperature for an additional 20 hr. At that point, the reaction mixture was filtered, the filtrate was concentrated, and the red oil, which remained, was chromatographed on neutral alumina (Woelm I) using cyclohexane–benzene (3:1) as eluent. After removal of all but about 1 ml of solvent, the remaining solution was analyzed by glpc. The chromatogram contained several large peaks in addition to the phenylphenanthrenes. The possibility that these might be dihydrophenylphenanthrenes is discounted in view of the failure of attempted dehydrogenations with *p*-chloranil and 10% Pd on charcoal.

**9-Acetonylanthracene.** To a 2-l., three-necked flask were added 1500 ml of acetone, 7.12 g (0.0267 mol) of anthracene, and 13.12 g (0.0533 mol) of *N*-nitrosoacetanilide with stirring under nitrogen. After the mixture was allowed to stand overnight, the solvent was removed and the residue was dissolved in benzene. This solution was chromatographed on 1 lb of acid-washed alumina (Merck). The column was eluted with 1:1 hexane–benzene until the first fluorescent band was removed. Continued elution with benzene gave a second fluorescent fraction that was rechromatographed on the same type of alumina with benzene. This chromatogram exhibited a yellow zone between two red bands. The former was collected and the benzene was removed. The residue was recrystallized from methanol using Norit. A total yield of 93 mg of product was isolated. The first crop was pure by glpc: mp 111–112°; uv max (95% ethanol) 255, 332, 348, 366, and 386 mμ; ir ($CCl_4$) 1724 cm$^{-1}$ (C=O); nmr ($CCl_4$) δ 1.85 (s, 3, $CH_3$), 2.16 (m, 9, aromatic), 4.45 (s, 2, $CH_2$).

*Anal.* Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02; O, 6.83; mol wt, 234. Found: C, 87.28; H, 6.12; O, 6.60; mol wt, 243.[50]

**NAA Phenylation of Benzene.** *N*-Nitrosoacetanilide (185 mg) was added to 50 ml of benzene preheated to 60° in a flask under nitrogen with rigorous stirring. Although the reaction was instantaneous, the mixture was allowed to stand overnight before the solvent was removed. The residue was redissolved in a small volume of benzene and analyzed by glpc. The chromatogram revealed the presence of a compound having the same retention time as 1,4-dihydrobiphenyl and amounting to about 3% of the biphenyl present. A sample of this compound collected from the gas chromatograph exhibited ir and uv absorption identical with those shown by authentic 1,4-dihydrobiphenyl.[51] This compound could not be detected by glpc among the products of the decomposition of NAA in benzene at room temperature.

**Instrumentation and Analyses.** Infrared spectra were determined on Baird Model 4–55 and Perkin-Elmer infracord and Model 337 spectrophotometers. Ultraviolet spectra were obtained on Beckman Model DK-2 and Cary 15 spectrometers. The nmr spectrum was determined on a Varian A-60 instrument.

Both F&M Scientific Corp. Model 500, with a thermal conductivity detector, and Series 810 flame ionization detectors were used for glpc. In conjunction with the latter instrument, areas were determined with a Disc integrator Model No. 201 from Disc Instruments, Inc.; with a former, a Keuffel and Esser Model 4236 polar planimeter was used. All of the data for biphenylene, pyrene, and most of that reported here for anthracene were obtained on the flame ionization unit. The total rate factors for phenanthrene were also measured with that instrument. Columns, conditions, and choice of internal standards are too numerous to record here. However, by way of example, M and NAA reactions of pyrene were analyzed for total rate factors with a pair of 4 ft × 1/8 in. stainless steel columns, packed with 10% SE-30 on 80–100 mesh Chromosorb P, using naphthalene, phenanthrene, and chrysene as internal standards. These columns gave no visible separation of 1- and 4-phenylpyrene but partial resolution was obtained on an identical pair of columns packed with 10% Versamid 900 on the same support. Another pair of these columns in lengths of 3 ft were used for analysis of the NAA phenylations of anthracene. In this connection, the report that the decomposition of NAA in the presence of anthracene yields small amounts of triptycene[52] prompted a check for possible interference in our analyses. However, it was found that triptycene is readily differentiated from anthracene and the phenylanthracenes by glpc.

(44) After synthesis of 9- and 1-phenylphenanthrene by the classical method of Haworth, a photochemical route to 9-phenylphenanthrene was published by F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist and M. L. Savitz, *J. Amer. Chem. Soc.*, 84, 4361 (1962). Details of the synthesis of 1-, 2-, 3-, and 4-phenylphenanthrenes by this superior method will be published elsewhere.

(45) Although it was not obvious from examination of the earlier literature, all three isomeric phenylpyrenes had in fact been synthesized by others prior to this study. For details, see S. C. Dickerman and W. M. Feigenbaum, *Chem. Commun.*, 345 (1966).

(46) W. Baker, A. J. Boulton, C. R. Harrison, and J. F. W. McOmie, *Proc. Chem. Soc., London*, 414 (1964).

(47) P. Walker, *J. Org. Chem.*, **26**, 2994 (1961).

(48) G. G. Petukhov, N. V. Likhovidova, and R. T. Galiulina, *Tr. Khim. Khim. Tekhnol.*, **4**, 682 (1961); *Chem. Abstr.*, **58**, 489*a* (1963).

(49) H. France, U. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 369 (1940).

(50) By the Schwarzkopf Microanalytical Laboratory, Woodside, New York 11377.

(51) Prepared by the method of W. Hückel and R. Schwen, *Chem. Ber.*, **89**, 150 (1956).

(52) D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Commun.*, 727 (1967).

**Acknowledgments.** Technical assistance from E. I. du Pont de Nemours and Co. through Mr. Wesley Dorsheimer and from Dr. Robert Gore of the Perkin-Elmer Corp. is gratefully acknowledged. We are also indebted to Professors M. S. Newman and F. B. Mallory for authentic samples of 2- and 9-phenylphenanthrenes, respectively, and to the latter for manuscript copy in advance of publication.

# A Microcalorimetric Determination of the Chair–Boat Enthalpy Difference in 1,3-Dioxane[1]

**R. M. Clay, G. M. Kellie, and F. G. Riddell***

*Contribution from the Department of Chemistry, University of Stirling, Stirling, Scotland.* *Received February 21, 1973*

**Abstract:** A microcalorimetric technique for the study of conformational equilibria in 1,3-dioxanes is introduced and applied to two systems. The chair → 1,4-twist enthalpy difference in 1,3-dioxane is found to be 37.3 kJ mol$^{-1}$.

Direct measurements of heats of reaction offer a most attractive and accurate means for studying conformational equilibria. Modern microcalorimeters are especially well suited for this since they enable extremely accurate measurement of heats of reaction even in quite dilute solutions. If a chemical equilibrium A ⇄ B can be readily established both from pure A and from pure B, then one can measure two heat changes, $\Delta H_1$ and $\Delta H_2$, as A and B, respectively, are converted into the equilibrium mixture.

It follows that

$$\Delta H_{A \rightarrow B} = \Delta H_1 - \Delta H_2$$

and the equilibrium constant ($K$) is given by

$$K = -\Delta H_2/\Delta H_1$$

Thus, all three thermodynamic parameters $\Delta G°$, $\Delta H°$, and $\Delta S°$ associated with the equilibrium may be determined.

It seemed to us that the 1,3-dioxane series, in which equilibria are readily established by Lewis acids,[2] would be especially amenable to study by this technique. One particular advantage offered by microcalorimetry is that it enables heat changes to be measured for the interconversion of the least stable isomer to the more stable isomer in cases where the equilibria are so one-sided as to prohibit accurate equilibrium studies. We, therefore, hoped that direct heat measurements for a twist → chair change would settle the question of the chair–boat energy difference in 1,3-dioxane for which values ranging from 9.2 to 35.5 kJ mol$^{-1}$ have been proposed (Table I).

**Table I.** Proposed Values of $\Delta H_{CT}$ for 1,3-Dioxane

| $\Delta H_{CT}$, kJ mol$^{-1}$ | Proposed by | Date | Ref |
|---|---|---|---|
| 9.2 | Eliel, Allinger, Angyal, and Morrison | 1965 | *a* |
| >12.5 | Anderson, Riddell, and Robinson | 1967 | *b* |
| >12.5 | Riddell and Robinson | 1967 | 3 |
| 25.9 | Anteunis and Swaelens | 1970 | *c* |
| 25.9 | Eccleston and Wyn-Jones | 1971 | *d* |
| 28.5 | Pihlaja | 1968 | *e* |
| 30.1 | Pihlaja and Luoma | 1968 | *f* |
| 30.1 | Eliel | 1971 | *g* |
| 33.4 | Eliel and Nader | 1970 | *h* |
| 35.5 | Pihlaja and Jalonen | 1971 | *i* |

[a] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965. [b] J. E. Anderson, F. G. Riddell, and M. J. T. Robinson, *Tetrahedron Lett.*, 2017 (1967). [c] M. Anteunis and G. Swaelens, *Org. Magn. Resonance*, **2**, 389 (1970). [d] G. Eccleston and E. Wyn-Jones, *J. Chem. Soc. B*, 2469 (1971). [e] K. Pihlaja, *Acta Chem. Scand.*, **22**, 716 (1968). [f] K. Pihlaja and S. Luoma, *Acta Chem. Scand.*, 2410 (1968). [g] E. L. Eliel, *Pure Appl. Chem.*, **25**, 509 (1971). [h] F. W. Nader and E. L. Eliel, *J. Amer. Chem. Soc.*, **92**, 3050 (1970). [i] K. Pihlaja and J. Jalonen, *Org. Mass. Spectrom.*, **5**, 1361 (1961).

## Experimental Section

The compounds employed were all prepared by accepted literature methods[3,4] and were purified prior to use through a 2-ft spinning band distillation unit. The purity of each compound was monitored by glc and nmr techniques and in all cases was >99%. All compounds had physical and spectroscopic properties in agreement with the literature.

An L. K. B. batch microcalorimeter with gold cells was used for the determination of thermochemical data. A Phillips chart recorder equipped with a Disc integrator enabled measurement of the peak areas with a maximum error of ±1%. In the case of 2,5-dimethyl-1,3-dioxanes, a 0.15 $M$ solution of the 1,3-dioxane in 1,4-dioxane and a 0.12 $M$ solution of $BF_3$ in 1,4-dioxane were used. For *trans*-2,4,4,6-tetramethyl-1,3-dioxane a 0.01 $M$ solution and a 0.02 $M$ solution of $BF_3$ in 1,4-dioxane were used.

Determinations (≤8) were carried out for each compound. For each determination *ca.* 1 ml of the 1,3-dioxane solution and a similar quantity of the $BF_3$ solution were weighed into the microcalorimeter. On completion of each experiment, the cell was washed once with a 10% solution of pyridine in chloroform, twice with dry chloroform, and finally twice with dry ether. (Compressed air was then blown through the cell to remove residual traces of solvents.) If this sequence was not employed, in particular if the cells were not washed with a basic solvent, reproducibility of results was extremely poor. All microcalorimetric work was performed at 298°K. Small corrections for the heat of dilution of each isomer were determined and applied to each measurement.

(1) Presented in part at the 27th Annual Calorimetry Conference (U. S. A.), Park City, Utah, July 1972.
(2) See, for example, E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970).
(3) F. G. Riddell and M. J. T. Robinson, *Tetrahedron*, **23**, 3417 (1967).
(4) E. L. Eliel, *Pure Appl. Chem.*, **25**, 509 (1971).