Mercuration of Naphthalene—Salient Features[1]

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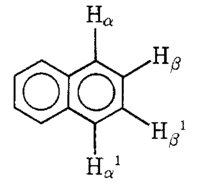
The mercuration of naphthalene by mercuric acetate in acetic acid (uncatalyzed) and under conditions of perchloric acid catalysis has been studied. Kinetically the reactions are first order in Hg(II) and in naphthalene, although under catalytic conditions some deviations from second-order behavior occur as the Hg(II) concentration is varied. The effects of added water, sodium perchlorate, and perchloric acid on the rates have been studied, and the results rationalized on the basis of certain acid–base reactions that are possible under these conditions, and delineated previously by Kresge and Brown. Naphthalene is mercurated very predominantly at the α position, based on a technique of accumulation of ^{199}Hg–^{1}H satellite intensity in the ^{1}H NMR spectra of the total product. The mercuration of naphthalene exhibits substantial isotope effects (k_H/k_D = 3.6 for uncatalyzed and 7.2 for $HClO_4$-catalyzed) and coupled with the kinetics, implicates a mechanism whereby the σ intermediate, in low concentration, is formed rapidly and reversibly from the Hg(II) electrophile and naphthalene, followed by rate-determining proton loss. Naphthalene, on a site for site basis, is more reactive at the α position than is benzene by factors of 11.7 (uncatalyzed) and 18.4 (catalyzed), in line with the low selectivity of this reaction. Some comments on the apparently high (α,β) positional selectivity but low substrate selectivity are made.

The mercuration reaction has been of considerable value in providing kinetic and isomer distribution data to test certain quantitative approaches to aromatic reactivity.[3,4] Considerable understanding of the mechanisms of aromatic mercuration has been achieved,[5–9] but very little information is available on even qualitative aspects of mercuration of aromatic systems other than benzene and substituted benzenes. Some years ago we conducted a thorough study of the mercuration of naphthalene by mercuric acetate in acetic acid, both "neutral" and catalyzed by perchloric acid,[1] at about the time Kresge and Brown[7–9] published their definitive mechanistic analyses of the mercuration of benzene. Consequently, we deferred publication of our results, but in view of recent interest in aromatic metalation reactions generally, and private requests for aspects of our data, we have decided to publish the salient features of the mercuration of naphthalene under various conditions, but to restrict mechanistic discussion, in view of Kresge and Brown's impressive previous reports.[7–9]

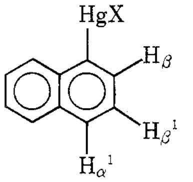
Results and Discussion

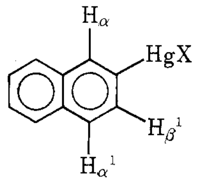
A. Isomer Distributions. We were stimulated by the reports[10,11] that mercuration of naphthalene under some conditions yielded substantial amounts of β isomer, and thallation of naphthalene with thallium(III) isobutyrate has been considered to be almost exclusively β, since only β-naphthylmercuric chloride was obtained by treatment of the naphthylthallium compound with mercuric chloride.[12] If these reactions were authentic electrophilic substitution, the above isomer distributions seemed odd for conditions of kinetic control, and prompted careful assessment of the isomer distribution in mercuration.

For isomer determinations, a number of approaches, including polarography, bromodemercuration, etc., were tried, but eventually we developed a new method based on computer accumulation of ^{199}Hg–^{1}H satellites (^{199}Hg is 16.8% naturally abundant; $I = \frac{1}{2}$) which allows direct observation of reaction products, and the method has general applicability to reactions of the present type where metal–^{1}H coupling occurs. The ^{1}H NMR spectrum of naphthalene has been analyzed as an A_2B_2 system,[13] which is valid if the A_4B_4 system is regarded as the superposition of two A_2B_2 sets, with inter-ring coupling ignored. In α-deuterionaphthalene it is the lower half of the initial mirror-image pattern that is of reduced intensity, so that H_α resonates at lower field. This spectrum closely resembles that of α-naphthylmercuric acetate or chloride (mercuric substituents exert feeble substituent effects)[14] so that the coupling constants found for naphthalene apply, for the present level of precision, to the naphthylmercurials. Thus it is possible to predict the effects of substituting HgX for H_α or H_β leading to α-$C_{10}H_7HgX$ or β-$C_{10}H_7HgX$, and in particular, the multiplicities of the ^{199}Hg satellites. In α-$C_{10}H_7HgX$, the satellites of H_β should appear basically as a broadened doublet since $J_{H_\beta-H_{\beta^1}} \sim 6$ and $J_{H_\beta-H_{\alpha^1}} \sim 1.4$ Hz, and in the spectrum of α-$C_{10}H_7HgCl$ (Me_2SO solvent) signals of appropriate intensity and multiplicity are located 112 Hz to the low- and high-field sides of the higher field component of the aromatic resonance. Thus $J_{Hg-H_\beta} \sim 224$ Hz. In β-$C_{10}H_7HgX$, the situation is simpler since now H_α is feebly coupled to $H_\beta{}^1$ ($J \sim 1.4$ Hz) so that H_α protrudes from the α portion of the aromatic resonance as a broadened singlet. Consequently, the ^{199}Hg satellites appear essentially as singlets and again $J_{Hg-H_\alpha} \sim 224$ Hz. Coupling to $H_\beta{}^1$ would also occur, and the satellites would each appear as broadened doublets as $J_{H_{\beta^1}-H_{\alpha^1}} \sim 6$ and $J_{H_{\beta^1}-H_\alpha} \sim 1.4$ Hz. There is some evidence for this on the downfield side of the main β resonance but distribution of intensity among four lines (or two broadened signals) makes it far less obvious than the H_α satellite. These situations are summarized in Figure 1 in a schematic fashion since the details of the main aromatic resonance pattern are not important to the argument.



$J_{H_\alpha-H_\beta}$ = 8.6 Hz
$J_{H_\alpha-H_{\beta^1}}$ = 1.4 Hz
$J_{H_\beta-H_{\beta^1}}$ = 6 Hz





Thus the low-field satellite pattern for a mixture of α- and β-$C_{10}H_7HgX$ would consist of a singlet (J_{Hg-H_α}) separated by ca. 15 Hz from two overlapping broadened dou-

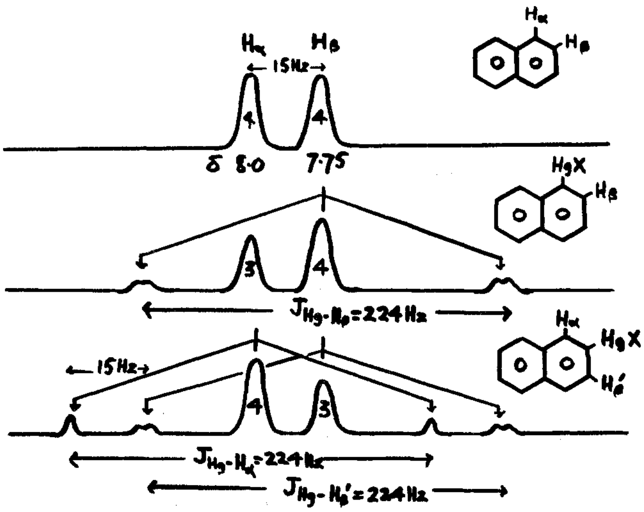
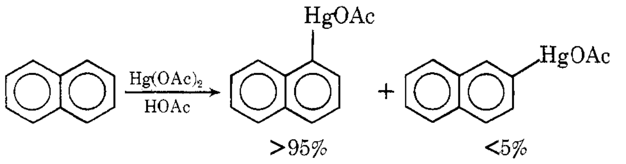


Figure 1. Schematic representation of ^1H spectral traces associated with naphthalene and the α- and β-naphthylmercury halides. The relative intensities of the main H_α and H_β resonances are indicated, and the flanking ^{199}Hg–H satellites shown for the two situations.

blets (J_{Hg-H_β} and $J_{Hg-H_{\beta^1}}$). Presence of substantial amounts of β isomer, therefore, would be indicated by the presence of both satellite regions while predominating α isomers would lack the characteristic satellite singlet (J_{Hg-H_α}). As described in the Experimental Section, the product acetates were precipitated as the chlorides and their ^1H NMR spectra in the low-field satellite region were continually scanned with the Varian computer of average transients (CAT) until a high satellite intensity was accumulated. The computer readouts are shown in Figure 2 and in a and b are the readouts for the uncatalyzed and $HClO_4$-catalyzed reactions. The large peak (now a broadened singlet in the readout) on the right hand side of each diagram is due to the α isomer, and indicated with a double asterisk. c and d are the readouts from reaction mixtures identical in composition and conditions of study, except for the addition of ~5% of β-naphthylmercuric acetate, after the completion of the reaction but prior to the precipitation as the chloride. The response due to the added β isomer is clearly seen as a pronounced peak downfield from the α resonance. The presence of β isomer is more noticeable as the amplitude is increased (upper trace), but clearly less than 5% of β-mercuration occurs in both the neutral and acid-catalyzed reactions. Intensity comparisons would suggest not less than 95% α-mercuration. This conclusion is also in harmony with kinetic isotope effects for naphthalene-d_8 and specifically deuterated naphthalenes (vide infra).



Under other conditions it does appear that substantial postkinetic $\alpha \gtrless \beta$ equilibration occurs. For example, Verwey and Kooyman report[10,11] that the reaction of $C_{10}H_8$ (1.23 mol) with $Hg(OAc)_2$ (0.005 mol) at 96 °C for 3 h leads to 65% α and 35% β substitution. It is of interest that we could not detect equilibration of the α isomer with the β after several half-lives of the substitution reaction at 70 °C. However, the different solvent system and temperature could account for this. The predominant formation of α product is in line with other authentic electrophilic substitutions in naphthalene, as bromination,[15] chlorination,[16] and nitration[17] yield α isomers to the extents of 99, 97, and 90%, respectively. These results are rationalized by rudimentary MO theory,[18] as L^+, the cationic localization energy, is related to the loss of π-election stabilization on forming the Wheland-type intermediate $C_{10}H_8E^+$. For β-substitution, $L^+ = 2.48\beta$, but 2.29β for α-substitution, thus favoring the latter. It may have been thought that the supposed "bulky" nature of metal electrophiles would be a factor operating against α-substitution, but the evidence is[19,20] that the steric requirements of HgOAc would be inconsequential.

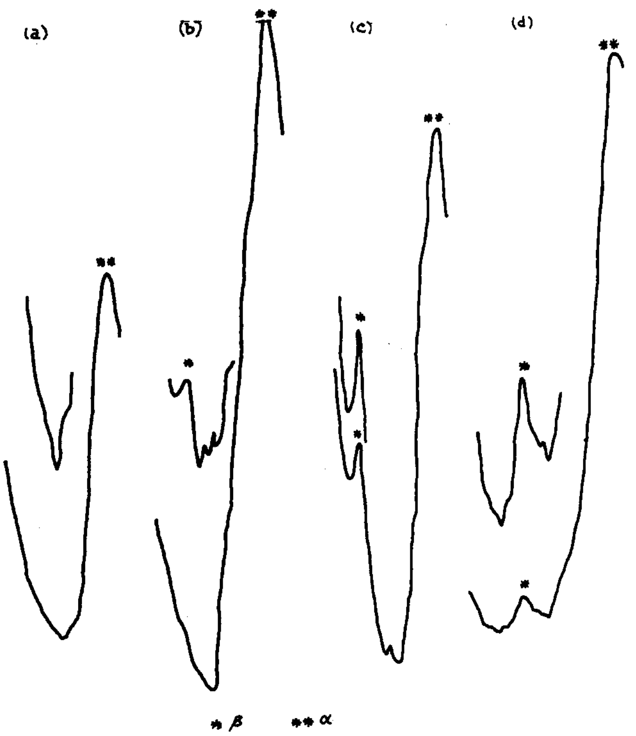
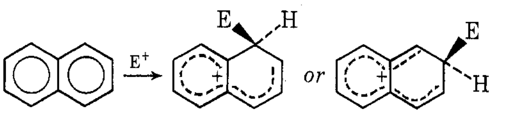


Figure 2. (a) Computer readout of low-field satellites region of product naphthylmercuric chlorides from the uncatalyzed reaction. (b) Similarly for $HClO_4$-catalyzed reaction. The large peak (**) is due to the α isomer, while that for the β isomer (*) is barely perceptible. (c) and (d) are the readouts corresponding to (a) and (b), respectively, except that 5% of β-acetomercurinaphthalene has been added after completion of reaction but prior to precipitation as the chloride. The response due to the β isomer is clearly seen (marked *) downfield from the α resonance, and indicates that less than 5% of β isomer was formed in direct mercuration.



Kinetics of Mercuration. A. $Hg(OAc)_2$ in Acetic Acid. The reactions were followed by the well-established thiocyanate titration technique[21] for unreacted Hg(II) and product RHg(II) species. The stoichiometry was established as $C_{10}H_8$:$Hg(OAc)_2$:1-acetatomercurinaphthalene = 1:1:1 on the basis of "infinity" titres after ca. 6 half-lives, under conditions with naphthalene in excess by at least a factor of 6 to avoid complicating polymercuration.[21] Under these conditions, plots of log $(2T_t - T_0)$ vs. time were satisfactorily linear, and pseudo-first-order rate constants were determined graphically (T_t = titre after time "t"; T_0 = titre at time zero). For varying concentrations of $Hg(OAc)_2$ and $C_{10}H_8$, division of the pseudo-first-order constant by $[C_{10}H_8]$ yielded acceptably invariant second-order rate

Table I. Results of Kinetic Studies of the Reaction of Naphthalene and Mercuric Acetate in Glacial Acetic Acid (Uncatalyzed)

I	II	III	IV	V	VI	VIII
No.	Temp, °C	[Naph], mol/l.	$[Hg(OAc)_2]$, mol/l.	$[H_2O]$, %	[NaOAc], mol/l.	$k_2 \times 10^3$, $mol^{-1}\ min^{-1}$
1	70	0.97	0.0919			2.67
2	70	0.97	0.092			2.67
3	70	0.98	0.1195			2.74
4	70	0.98	0.1190			2.74
5	70	0.928	0.089			2.78
6	70	0.928	0.0875			2.78
7	70	1.875	0.12			2.70
8	70	1.875	0.125			2.70
9	70	1.5	0.1035			2.725
10	70	1.5	0.1025			2.725
11	70	0.588	0.0950			3.02
12	70	0.588	0.0966			3.02
13	70	0.997	0.113	5.75		3.14
14	70	0.997	0.113	5.75		3.14
15	70	0.996	0.113	5.75	0.114	2.91
16	70	0.997	0.113	5.75	0.114	2.91
17	60	0.871	0.108			1.132
18	60	0.871	0.0995			1.132
19	80	0.838	0.1009			6.07
20	80	0.838	0.1005			6.07

constants. Thus the reaction is first order in both $C_{10}H_8$ and Hg(II). The details are assembled in Table I.

A very slight acceleration accompanies an increase in the water content (run 13), while addition of NaOAc under these conditions causes a slight retardation (run 15). A number of factors may be associated with these altered conditions, but the effects are so small that meaningful analysis is not possible. There seems no reason to doubt that the electrophile under these conditions is very largely un-ionized mercuric acetate.

The temperature variation of k_2 is also shown in Table I and in standard fashion, a plot of log k_2 vs. $1/T$ yielded a value of the energy of activation, E_a, of 17.8 kcal/mol with $\Delta H^{\ddagger} = 17.2$ kcal/mol at 25 °C.

The rate data in Table I may be compared with those available for benzene,[21] and α-mercuration is ca. 11.7 times as fast as mercuration at a single benzene position. This is remarkably low, when compared with nitration and chlorination, where reactivity ratios of ca. 470 and 10^5 are observed,[22] demonstrating the low selectivity[3] of uncatalyzed mercuration.

B. $Hg(OAc)_2$ in Acetic Acid Catalyzed by Perchloric Acid. As noted by Westheimer[6] and investigated in great detail by Kresge and Brown,[7-9] $HClO_4$ strongly catalyzes the mercuration of benzene. In the case of naphthalene, accelerations of comparable magnitude are observed, and, for example, at 70 °C (extrapolated from data at lower temperatures) mercuration in the presence of 0.115 M $HClO_4$ and 0.55 M H_2O proceeds ca. 1440 times faster than the uncatalyzed reaction. The essential aspects of our kinetic data are shown in Table II. The stoichiometry of the catalyzed reaction was established as outlined earlier. A comparison of entries 8, 9, 12, 13, 14, and 15 in Table II in which the only variable is $[C_{10}H_8]$ shows that the k_2 values, calculated as before, are essentially invariant over the range studied. Thus first-order dependence in $C_{10}H_8$ is again established. Deviation from strict first-order behavior was observed when the initial $[Hg(OAc)_2]$ was altered, with other conditions constant. This follows from runs 1, 14, and 15 where a significant increase in k_2 is observed when $[Hg(OAc)_2]$ is halved.

Runs 1–6 in Table II show a definite positive linear dependence on perchloric acid concentration, as has been observed previously for the benzene system. The equilibrium

$$HClO_4 + Hg(OAc)_2 \rightleftharpoons {}^{+}HgOAc\ ClO_4^{-} + HOAc \qquad (A)$$

has been regarded[7] as responsible, producing a more potent mercurating agent. Dampening this effect somewhat is the presence of water, since its weakly basic nature in acetic acid allows interaction with and competition for the available $HClO_4$.

$$H_2O + HClO_4 \rightleftharpoons H_3{}^{+}O\ ClO_4^{-}$$

It is clear from the work of Brown and Kresge[7] that under these conditions ${}^{+}HgOAc\ ClO_4^{-}$ is the major mercurating agent, with perhaps small contributions from mercuric perchlorate ion triplets $Hg^{2+}(ClO_4^{-})_2$, and un-ionized-$Hg(OAc)_2$. However it can be calculated that at 20 °C, the rate constant for substitution by $Hg(OAc)_2$ is ca. 2×10^{-5} $mol^{-1}\ min^{-1}$, and therefore the observed rate of $(3–28) \times 10^{-3}$ must arise predominantly from a reaction between acetatomercuric perchlorate ion pairs and naphthalene.

The positive deviation from second-order behavior mentioned above has been noted by Kresge, Dubeck, and Brown[7] and explained in terms of the consequence of lowering $[Hg(OAc)_2]$ on the equilibrium A above.

Runs 20–25 indicate an approximate linear relation between k_2 and $[NaClO_4]$, and this is associated with the solvolysis of $NaClO_4$, to produce a significant concentration of $HClO_4$.

$$NaClO_4 + HOAc \rightleftharpoons NaOAc + HClO_4 \ (K \sim 6 \times 10^{-5}\ M \text{ for } 0.1\ M \text{ salt})$$

This acid then converts enough $Hg(OAc)_2$ to ${}^{+}HgOAc\ ClO_4^{-}$ to provide the observed rate accelerations.

Under standard conditions[9] at 25 °C where $[HClO_4]_{anal} = 0.50$ M and $[H_2O]_{anal} = 0.20$ M, naphthalene is 12.3 times as reactive as benzene. As $HClO_4$-catalyzed mercuration is essentially exclusively α, this α-substitution is ca. 18.4 times as facile as at a single benzene position. The catalyzed reaction has been shown to be more discriminating,[9] and discussion[9] of this unusual phenomenon is available.

Kinetic Isotope Effects. Large primary isotope effects

Table II. Results of the Kinetic Study of the Reaction between Naphthalene and Mercuric Acetate in Acetic Acid (ca. 99%) Catalyzed by Perchloric Acid

I	II	III	IV	V	VI	VII	VIII
No.	Temp, °C	[Naph], mol/l.	$[Hg(OAc)_2]$, mol/l.	$[H_2O]$, mol/l.	$[HClO_4]$, mol/l.	$[NaClO_4] \times 10^2$, mol/l.	$k \times 10^2$, mol^{-1} min^{-1}
1	20	0.532	0.116	0.554	0.1129		2.31
2	20	0.532	0.116	0.561	0.0921		2.115
3	20	0.532	0.116	0.55	0.0922		2.19
4	20	0.532	0.116	0.56	0.069		1.225
5	20	0.532	0.116	0.546	0.0502		0.93
6	20	0.532	0.116	0.604	0.0247		0.242
7	20	0.532	0.116	0.548	0.0215		0.32
8	20	0.274	0.0508	0.55	0.11		2.76
9	20	0.281	0.0508	0.55	0.11		2.79
10	20	0.399	0.0508	0.567	0.0467		0.794
11	20	0.397	0.051	0.556	0.0461		0.798
12	20	0.399	0.051	0.55	0.11		2.78
13	20	0.398	0.051	0.55	0.11		2.72
14	20	0.532	0.051	0.55	0.115		2.81
15	20	0.532	0.051	0.55	0.115		2.81
16	24	0.532	0.0508	0.55	0.115		4.30
17	24	0.532	0.051	0.55	0.115		4.39
18	28	0.532	0.0508	0.55	0.115		6.90
19	28	0.532	0.0509	0.55	0.115		6.95
20	70	1.00	0.101			0.1	4.11
21	70	1.00	0.101			0.1	4.12
22	70	1.00	0.101			0.2	5.50
23	70	1.00	0.101			0.2	5.52
24	70	1.00	0.101			0.3	6.81
25	70	1.00	0.101			0.3	6.78

Table III. Results of Kinetic Studies of Deuterium-Labeled Naphthalenes with Mercuric Acetate in Glacial Acetic Acid at 70 ± 0.05 °C

No.	Substrate	[Substrate], mol/l.	$k_2 \times 10^4$, mol^{-1} min^{-1}	Kinetic isotope effect
1a	Naphthalene-h_8	0.867	29.3	
b	Naphthalene-d_8	0.867	8.4	3.49
2a	Naphthalene-h_8	0.854	28.0	
b	Naphthalene-d_8	0.854	7.6	3.68
3a	Naphthalene-h_8	0.854	28.8	
b	Naphthalene-*1*-d_1	0.856	22.1	1.305 (1.21)
c	Naphthalene-*1,4*-d_2	0.854	20.7	1.39 (1.56)
4a	Naphthalene-h_8	0.89	27.4	
b	Naphthalene-*1*-d_1	0.875	21.5	1.272 (1.22)
c	Naphthalene-*1,4*-d_2	0.889	16.5	1.66 (1.56)

Table IV. Results of Kinetic Studies of Deuterium-Labeled Naphthalenes with Mercuric Acetate in 99% Acetic Acid at 20 ± 0.01 °C, Catalyzed by Perchloric Acid[a]

No.	Substrate	[Substrate], mol/l.	$k_2 \times 10^3$, mol^{-1} min^{-1}	Kinetic isotope effect
1a	Naphthalene-h_8	0.425	21.75	
b	Naphthalene-d_8	0.425	2.95	7.35
2a	Naphthalene-h_8	0.425	21.75	
b	Naphthalene-d_8	0.425	3.02	7.2
3a	Naphthalene-h_8	0.425	21.75	
b	Naphthalene-*1*-d_1	0.425	18.4	1.17 (1.27)
c	Naphthalene-*1,4*-d_2	0.425	12.6	1.725 (1.75)
4a	Naphthalene-h_8	0.425	21.75	
b	Naphthalene-*1*-d_1	0.425	19.35	1.12 (1.27)
c	Naphthalene-*1,4*-d_2	0.425	15.32	1.44 (1.75)

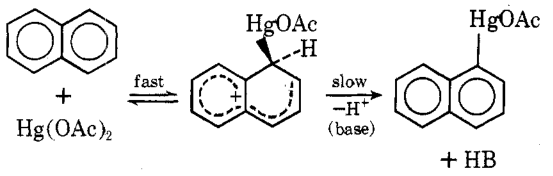
[a] Perchloric acid concentration 0.0995 M; water concentration 0.553 M.

have been recorded for uncatalyzed mercuration of benzene by $Hg(OAc)_2$ ($k_H/k_D \sim 3.2$)[23] and under $HClO_4$ catalysis[8] ($k_H/k_D = 6.0$) at 25 °C. In the latter situation reaction occurs via $^+HgOAc\ ClO_4^-$ (90%) and $Hg^{2+}\ (ClO_4^-)_2$ (10%). In our work, mercurations of 1-deuterionaphthalene, 1,4-dideuterionaphthalene, and naphthalene-d_8 were studied under both catalyzed and uncatalyzed conditions. In Table III the results for uncatalyzed mercuration are listed.

From 1a, 1b and 2a, 2b a primary isotope effect of 3.6 ± 0.1 is associated with the substitution, if secondary effects are neglected. Placing reliance in this data, it is possible to calculate what the observed ratio of rate constants for ($C_{10}H_8$, 1-D-$C_{10}H_7$) and ($C_{10}H_8$, 1,4-D_2-$C_{10}H_6$) should be if α-substitution is as exclusive as we concluded earlier. The calculated values are shown in parentheses and the agreement is very reassuring indeed.

Under conditions of $HClO_4$ catalysis, the kinetic isotope effects are substantially larger (7.3 ± 0.1) and the data are assembled in Table IV. Again calculated ratios for the 1-D and 1,4-D_2 systems are shown in parentheses and the agreement is not as impressive as for the uncatalyzed cases.

The mechanistic significance of these large kinetic isotope effects in mercuration has been discussed in detail by Kresge and Brennan[8] and as the mercuration is first order in $C_{10}H_8$ under our conditions, the transition state of the slowest step contains a molecule of $C_{10}H_8$. These results together are consistent with rapid and reversible combination of electrophile and naphthalene to form a σ complex in low concentration from which proton loss is rate determining. For uncatalyzed mercuration, the electrophile has been



demonstrated[7] to be predominantly un-ionized $Hg(OAc)_2$ while the base is probably acetic acid solvent. For the catalyzed reaction a more complex mechanistic situation would exist, as delineated by Kresge and Brown,[7-9] but again proton loss from a σ complex, present in low concentration, would be rate determining. The larger k_H/k_D values for the naphthalene system may be associated with greater stabilization of the naphthalene σ intermediate.

Positional and Substrate Selectivity. Aromatic mercuration[3,7-9] is known to be a reaction of low selectivity compared with, for example, chlorination,[22] and the rather small rate differential between benzene and naphthalene is therefore not surprising. However, on this basis, it may have been anticipated that significant amounts of both α and β isomers would have been formed, but determinations indicate not less than 95% α product. Comparison of positional and substrate selectivities (benzene vs. α, and β in naphthalene) for mercuration and, for example, chlorination is difficult, because aromatic mercuration is located toward the other end of the mechanistic spectrum usually considered to describe aromatic electrophilic substitution,[9] i.e., proton removal, is largely, if not completely, rate determining. Therefore, both the ratio (k_1/k_{-1}), regulating the concentration of σ intermediate, and k_2, describing proton loss, are important ($k_{-1} \gg k_1 > k_2$) and act in antagonistic fashion. That is, the α σ intermediate, presumably more stable, will be less prone to deprotonate compared with the β σ intermediate. Other factors, such as accessibility of base for deprotonation, differing degrees of C–Hg hyperconjugative stabilization for the two σ intermediates, etc., are likely to be important in a subtle and finely balanced situation. It requires only a relatively small energy difference to change the relative (α,β) rates so that the isomer distribution is substantially altered. (The evidence is that the α mercurial is less stable thermodynamically than β.)[10]

Conclusions

The mercuration of naphthalene by mercuric acetate in acetic acid with and without $HClO_4$ catalysis provides predominantly α-naphthylmercury product. The general features of the reactions parallel those reported for mercuration of benzene, and in particular pronounced $HClO_4$ catalysis and kinetic (hydrogen) isotope effects are observed. Naphthalene is more reactive (on a site for site basis) at the α position by factors of 11.7 (uncatalyzed) and 18.4 (catalyzed). These results confirm the generally low selectivity of the mercuration reaction.

Experimental Section

Reagents. Acetic acid was purified by refluxing with chromium trioxide until the solution remained permanently orange, indicating the removal of all oxidizable material. The acid was then distilled through glass halices in a glass-walled, vacuum-jacketed column (42 × 1 in.) using a reflux ratio of 8:1. Precautions were taken to exclude atmospheric moisture, and the acid was redistilled from mercuric acetate just prior to the kinetic runs.

Mercuric acetate (May and Baker Ltd.) was used without further purification (Found: C, 15.05; H, 1.88. Calcd for $C_4H_6HgO_4$: C, 15.09; H, 1.89). Perchloric acid [70%, specific gravity 1.70 (BDH Ltd.), Analytical Reagent Grade] was used as supplied. Sodium perchlorate (Ajax Chemicals Ltd., Univar, AR Grade) was dried at 110 °C for 4 h. Naphthalene (BDH) was refluxed for 72 h under N_2 over molten sodium. The naphthalene was then distilled and twice recrystallized from absolute ethanol and finally dried in a current of nitrogen, mp 80.5 °C (lit. 80.8 °C). Naphthalene-d_8 (Merck Sharp and Dohme of Canada Ltd.) was used as supplied. Naphthalene-*1*-d_1 and naphthalene-*1,4*-d_2 were synthesized according to Renaud and Leitch.[24] Mass spectral analysis provided the following.

		$C_{10}H_6D_2$, %	$C_{10}H_7D$, %	$C_{10}H_8$, %
Naphthalene-*1*-d_1	(a)		100	
	(b)		97	3
Naphthalene-*1,4*-d_2	(a)	99.5	0.5	
	(b)	95.5	4.5	

1-Chloromercurinaphthalene was made by the method of Blicke and Smith[25] and had mp 190–192 °C (lit. 188–190 °C). 2-Chloromercurinaphthalene was made by treatment of the double salt 2-diazonaphthylmercuric chloride with copper powder in a modified Sandmeyer reaction.[26] The acetatomercurinaphthalenes were made by treatment of the bis(naphthyl)mercury compounds with an equimolar amount of mercuric acetate in THF. The acetates were recrystallized from methanol to yield fine needles of 1-acetatomercurinaphthalene, mp 156–159 ° (lit. 154 °C),[27] and 2-acetatomercurinaphthalene, mp 148–150 °C (Found: C, 37.18; H, 2.57. Calcd for $C_{12}H_{10}HgO_2$: C, 37.25; H, 2.68). The ^1H NMR spectra (CH_2Cl_2 solvent δ 5.32) confirm the structures. The α isomer exhibits signals at δ 2.17 (3 H) $OCOCH_3$; 7.32–7.65 (4 H, complex) β protons; 7.70–8.22 (3 H, complex) α protons. For the β isomer signals are observed at δ 2.17 (3 H) $OCOCH_3$; 7.32–7.72 (complex, 3 H) β protons; 7.75–8.05 (complex, 4 H) α protons. A prominent "broad" singlet at δ 7.82 is assigned to H_1 in this β compound, since it experiences no ortho coupling. These spectra are consistent with the facts that (a) β protons resonate at higher field than α protons in naphthalene[13] and (b) the –HgOAc group has a feeble electronic effect.[14]

The bis(naphthyl)mercury compounds used in the above syntheses were made from the corresponding chloromercurinaphthalenes by symmetrization with an eight molar ratio of sodium iodide in acetone.[28]

Kinetics. The thiocyanate titration technique[21] was employed for following the reactions, and is based on the fact that Hg(II) consumes 2 equiv of SCN^-, whereas the product RHg(II) consumes but one. It is easy to demonstrate that, under conditions with $C_{10}H_8$ in large excess (>6 molar ratio) log $(2T_t - T_0)$ vs. time should be linear for a first-order dependence on Hg(II). T_t is the KSCN titre at time t, and T_0 at time zero. The large excess of $C_{10}H_8$ avoided the significant onset of complicating polymercuration. The pseudo-first-order rate constants were obtained graphically and converted to second-order constants by dividing by the essentially invariant $[C_{10}H_8]$. Rate constants are considered accurate to 5%. The procedure used in a typical run, regarding preparation of kinetic solution, titration technique, etc., have been described in detail by Brown and Kresge.[7-9] The reactions were generally followed for at least 2 half-lives, and at least duplicated. For determination of the kinetic isotope effect, simultaneous runs involving deuterated and regular substrate were conducted. Water concentrations were estimated by the Karl Fischer technique.

The products from the reaction were identified by ^1H NMR spectroscopy and comparisons with authentic samples of the α- and β-naphthylmercuric chlorides and acetates, as described below.

Isomer Distributions. Mixtures of naphthalene and $Hg(OAc)_2$ were allowed to react under the conditions employed in the kinetic studies. After ca. 90% reaction had occurred, the reaction mixture was quenched by pouring into aqueous sodium chloride. The precipitate was filtered and dried, and the dried precipitate evacuated at 100 °C and 10^{-1} mmHg for 3 h to remove the majority of the unreacted naphthalene. The mixture of product halides and residual naphthalene was dissolved in dimethyl sulfoxide in which the arylmercuric chlorides are extremely soluble. (~5 M). The ^1H NMR spectra were then analyzed in the region 100–130 H downfield from the aryl resonance, using a Varian A-60 spectrometer and a Varian CAT. Analysis of isomer distribution for the $HClO_4$-catalyzed reaction was estimated similarly. It was found by treatment of standard mixtures in exactly the same manner, the method was sensitive to less than 3% of β isomer.

Registry No.—Naphthalene, 91-20-3; mercuric acetate, 1600-27-7; 1-acetatomercurinaphthalene, 32049-36-8; 2-acetatomercurinaphthalene, 38487-16-0.

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Coupling of Nonequivalent Aromatic Rings by Soluble Nickel Catalysts. A General Route to the 1,8-Diarylnaphthalenes[1a]

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A facile route to the 1,8-diarylnaphthalene derivatives is described. The parent compound, 1,8-diphenylnaphthalene, can be prepared in two steps with 35% overall yield from the commercial 1,8-diaminonaphthalene. The key step in these preparations is the direct joining of two nonequivalent aromatic molecules by an organonickel-catalyzed Grignard–aryl halide coupling reaction at −15 °C. The coupling reaction is regiospecific with respect to the position of substitution of both aromatic halves. The yields of this coupling reaction are high, even though the 1,8-diarylnaphthalenes are sterically crowded. The efficiency of the reaction under a variety of conditions is evaluated. The order of reactivity of aryl halides is found to be I > Br > Cl, and it is possible to effect coupling preferentially at an iodo group in the presence of a chloro group, the latter being available for further synthetic functionalization.

The 1,8-diarylnaphthalenes are of interest because of their unusual geometry and their inherent strain due to steric overcrowding. The crowded peri-aryl rings are constrained to face each other.[2] Adjacent parallel π systems are also a feature of the extensively studied[3a] paracyclophanes, though the phenyl rings of the latter are substantially warped from planarity,[3b] while the aryl rings of the diarylnaphthalenes, which are not bound together at both ends, retain their planarity.[2] Many unusual properties have been observed with the paracyclophanes and these have been related to the closely held parallel aromatic ring geometries.[3a]

The 1,8-diarylnaphthalenes have, at the same time, π systems which are nearly perpendicular, because the naphthyl and peri-aryl ring planes are restricted from approaching coplanarity. The barrier to a 180° rotation about a naphthyl–aryl bond has been measured[4] as ~15 kcal which seems surprisingly low judging from examination of molecular models. The distance between atoms 1 and 8 in naphthalene is 2.44 Å, while the van der Waals separation between parallel π systems is 3.4 Å.[5] Thus, substantial repulsive interactions must exist between the peri-aryl substituents.[2]

We have undertaken a series of investigations of the conformational, thermodynamic, spectroscopic, and chemical properties of 1,8-diarylnaphthalene derivatives, which necessitated development of a convenient and efficient general synthesis for this class of compounds.[2b,6–9] The most straightforward approach envisioned was a direct joining of aryl and naphthyl groups, but preparative techniques for effecting carbon–carbon bond formation between two aromatic rings are notably lacking. Major classical methods for aromatic arylation are outlined below.

I Ullman reaction[2a,10] $2\mathrm{ArI} \xrightarrow{\mathrm{Cu}} \mathrm{Ar—Ar}$

II Scholl reaction[11] $2\mathrm{ArH} \xrightarrow[\mathrm{H^+}]{\mathrm{AlCl_3}} \mathrm{Ar—Ar}$

III Radical-mediated coupling[12]

$$\left.\begin{array}{l}[\mathrm{Ar—N_2}]^+ \\ \mathrm{Ar—N{=}N—Ar} \\ [\mathrm{Ar—CO_2}]_2 \\ \mathrm{Ar—I},\ h\nu \\ \text{or other radical source}\end{array}\right\} + \mathrm{Ar'H} \longrightarrow \mathrm{Ar—Ar'}$$

IV Benzyne-mediated coupling[13]

$$\begin{array}{c}\mathrm{Ar—X} \\ + \\ \mathrm{Ar'—Li}\end{array} \longrightarrow \begin{array}{c}\text{benzyne} \\ (\text{from Ar—X}) \\ \big\downarrow \mathrm{Ar'Li} \\ \mathrm{Ar—Ar'}\end{array}$$