was evaporated to dryness to leave *ca.* 0.5 g. of solid residue. This gave a negative test for mercuric chloride (or *trans*-2-methoxycyclohexylmercuric chloride) by the procedure described above.

Tests for Exchange between Mercuric Chloride and Alkylmercuric Chlorides.—To 1.5 g. (0.0043 mole) of *cis*-2-methoxycyclohexylmercuric chloride in *ca.* 40 ml. of ethyl ether was added 1.0 g. (0.0037 mole) of labeled mercuric chloride. The mixture was heated to dissolve the reactants and left at room temperature for 6 days, after which time it was evaporated to dryness. The solid obtained was treated with 30 ml. of 10% sodium hydroxide solution with stirring for about 30 minutes, to convert the mercuric chloride into insoluble mercuric oxide and the alkylmercuric chloride into the water-soluble hydroxide. After the mercuric oxide was separated by centrifugation, the mother liquor was added to 10 g. of lithium chloride in water and neutralized with 6 *N* acetic acid, precipitating *cis*-2-methoxycyclohexylmercuric chloride. After filtering, washing with water, and air drying at 40° for several hours, this product weighed 1.3 g. Recrystallization from 30 ml. of methanol–acetone (5 to 1) gave 1.0 g. (67%) of large crystals, m.p. 110.8–113.8°, whose radioactivity is shown in Table I.

Labeled mercuric chloride (1.0 g., 0.0037 mole) was allowed to react with *trans*-2-methoxycyclohexylmercuric chloride (3.0 g., 0.0086 mole) and the product was isolated by the method described above for the *cis* compound. (It was necessary to add 25 ml. of acetone to the reaction mixture to dissolve the reactants.) The 2.7 g. of crude *trans*-2-methoxycyclohexylmercuric chloride recovered was recrystallized from 20 ml. of chloroform–Skellysolve B to yield 1.3 g., which was then recrystallized from 15 ml. of 95% ethanol to give 1.05 g. (34%) of colorless crystals, m.p. 115.3–116.8°, whose radioactivity is shown in Table I.

Labeled mercuric chloride (1.0 g., 0.0037 mole) was dissolved in 40–50 ml. of ethyl ether containing 1.3 g. (0.0035 mole) of neophylmercuric chloride and the solution was allowed to stand 6 days at room temperature. This solution was evaporated to dryness and the resulting solid treated with 10% sodium hydroxide. The mercuric chloride was converted to the oxide, but only a very small amount of the neophylmercuric chloride dissolved. The solid mixture was separated, dried, and the neophylmercuric chloride extracted from the mercuric oxide with chloroform. The extract was evaporated to dryness and the resulting solid recrystallized from ethyl acetate–Skellysolve B. (The finely divided mercuric oxide was difficult to separate by filtration and probably accounts for the small residual radioactivity of the product.) The recrystallized neophylmercuric chloride weighed 0.4 g., the radioactivity being shown in Table I.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Mechanisms of Reaction of Organomercurials. II. Electrophilic Substitution on Saturated Carbon. Acetolysis of Dialkylmercury Compounds

BY S. WINSTEIN AND T. G. TRAYLOR[1]

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Acetolysis of dialkylmercuries has been investigated as an example of electrophilic substitution on carbon. Good first-order kinetics have been observed for the conversion of R_2Hg to RH and RHgOAc in the case of the diphenyl, di-*s*-butyl, di-*n*-butyl and dineophyl derivatives. Acetolysis stops cleanly with cleavage of the first alkyl group, cleavage of the second group being extremely slow. With dineophylmercury, addition of sodium acetate does not affect acetolysis rate, but inclusion of perchloric acid introduces a rapid second-order acidic acetolysis mechanism. In the neutral acetolysis, relative rates give the rate sequence, $(C_6H_5)_2Hg > (s\text{-Bu})_2Hg > (n\text{-Bu})_2Hg > (\text{neophyl})_2Hg$, qualitatively similar to the sequence in triiodide ion cleavage of RHgI. Probable mechanisms for neutral and acidic acetolysis of R_2Hg are discussed along with some of the factors determining rate of electrophilic substitution on carbon.

The acid cleavage of alkylmercury compounds is of interest as an example of electrophilic substitution on carbon.[2] In the case of hydrogen chloride cleavage, unsymmetrical diorganomercury compounds have been studied extensively by Kharasch and co-workers[3] and by Whitmore.[4] What we would now call an S_E1 mechanism was suggested by Kharasch for this cleavage. However, typical substances clearly do not follow an S_E1 mechanism, but one which requires concerted attack on carbon by the proton donor. The rate of cleavage depends on the presence and the nature of the electrophilic proton donor.[5,6]

Our original plan for the study of electrophilic substitution of organomercury compounds by acids was to measure the rates of reaction of acids with alkylmercuric salts. In this way the HgX moiety of RHgX could be kept constant and secondary effects due to changes in X would not be superimposed on the effects of structural changes in R. However, preliminary work showed that alkylmercuric salts reacted too slowly for rate measurement with glacial acetic acid, or with other non-halogen acids in water and acetic acid as solvents.[6] Alkylmercuric bromides reacted readily with hydrogen bromide in acetic acid, but a study of the kinetics of this reaction and the effects of peroxide and hydroquinone proved this reaction to go completely by a radical path.[6] On the other hand, dialkylmercury compounds react at convenient rates with glacial acetic acid. The kinetics of acetolysis of several dialkyl mercury compounds have been investigated, partly preliminary to stereochemical study. The kinetic study is reported in the present paper.

Corwin and Naylor[5] previously have reported an investigation of the kinetics of the reaction of diphenylmercury (I) with dioxane–acetic acid or dioxane–formic acid mixtures. Following the reaction dilatometrically, these authors observed that the reaction is unaffected by peroxides, faster with formic than acetic acid, first order in diphenylmercury (I) within a run, and slightly less than first order between runs. A typical electrophilic aro-

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[1] U. S. Rubber Co. Fellow, 1951-1952.

[2] S. Winstein, T. G. Traylor and C. S. Garner, THIS JOURNAL, **77**, 3741 (1955).

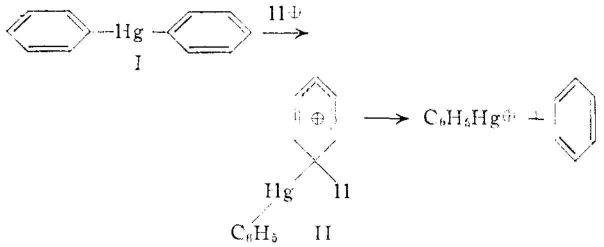
[3] M. S. Kharasch and R. Marker, *ibid.*, **48**, 3130 (1926).

[4] F. C. Whitmore and H. Bernstein, *ibid.*, **60**, 2626 (1938).

[5] *E.g.*, A. H. Corwin and M. A. Naylor, *ibid.*, **69**, 1004 (1947).

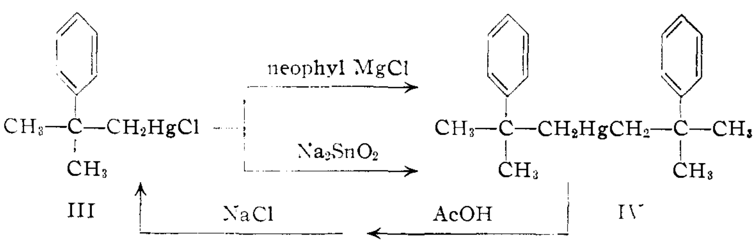
[6] (a) J. L. Keller, Dissertation, U.C.L.A., 1948; (b) S. Winstein, Paper at Organic Reaction Mechanisms Conference, Northwestern University, Evanston, Ill., Aug. 31, 1950.

matic substitution mechanism involving a Pfeiffer–Wizinger[7] (benzenium[8] ion, σ-complex[9]) intermediate II was suggested.[10] To compare our rates of electrophilic substitution on saturated carbon with the rate of electrophilic aromatic substitution, we included diphenylmercury (I) in the present investigation.



Results

Of the four organomercurials investigated, three, namely, diphenyl-, di-*s*-butyl- and di-*n*-butylmercury, were known substances. The fourth, dineophylmercury (IV) was prepared through the action of neophylmagnesium chloride on neophylmercuric chloride (III), and also through the action of sodium stannite on neophylmercuric chloride (III).



The mercurials reacted with acetic acid at convenient rates according to equation 1. From three of the cases, the alkylmercuric salt was isolated in good yield either as the acetate or as the chloride, and the results are summarized in Table I.

TABLE I

PRODUCTS OF SOLVOLYSIS

Compound	Temp., °C.	No. of half-lives	Compound isolated	Yield, %
$(C_6H_5)_2Hg$	25	30	C_6H_5HgOAc	88
$(n\text{-}C_4H_9)_2Hg$	75	11	$n\text{-}C_4H_9HgCl$	94
$[C_6H_5C(CH_3)_2CH_2]_2Hg$	100	20	$C_6H_5C(CH_3)_2CH_2HgCl$	89

The acetolysis rates could be followed by titration of the alkylmercuric acetate produced by a method developed by Keller.[6] This method involved neutralization of the alkylmercuric acetate with standard hydrogen bromide in glacial acetic acid using the brom phenol blue end-point (equation 2). While the method is accurate to *ca.* 0.1% for alkylmercuric acetate or mercuric acetate, some difficulty was experienced in the titration of solution aliquots containing unsolvolyzed dialkylmercury. At the titration end-point, where no more alkylmercuric acetate was present, the hydrogen bromide reacts very rapidly with dialkylmercury, causing fading end-points. Considerable improvement was obtained by inclusion of hydroquinone, which was known already to retard the reaction between hydrogen bromide and alkylmercuric bromide.[6]

$$RHgR + HOAc \longrightarrow RH + RHgOAc \qquad (1)$$

$$RHgOAc + HBr \longrightarrow RHgBr + AcOH \qquad (2)$$

The several substances displayed good first-order behavior in acetolysis. Typical runs are illustrated in Table II for diphenylmercury (I) and in Table III for di-*n*-butylmercury. With di-*n*-butyl- and dineophylmercury (IV), some of the runs were followed past 85% reaction and no drifts in rate constant were observed. The reaction is simplified by the relative resistance to cleavage of the second radical of the dialkylmercury, and this resistance is well illustrated in the kinetic work by the constancy of infinity titers from 10 to 20 or more reaction half-lives.

In acetolysis of dineophylmercury (IV), the effects of added sodium acetate or perchloric acid were investigated. The inclusion of equimolar sodium acetate changed the rate constant from 1.02×10^{-5} to 0.95×10^{-5} sec.$^{-1}$, by no more than the combined experimental errors. However, the inclusion of perchloric acid gave a very large increase in rate.

The solvolysis in the presence of perchloric acid is complicated by oxidation of the solvent by the neophylmercuric salt which is produced.[6] This is evidenced in the present work by an increase in acid concentration accompanied by precipitation of mercury droplets in the reaction mixture, both becoming appreciable after 40 to 50% reaction. However, this effect is small in the first 25%, and the present procedure was to employ relatively low concentrations of perchloric acid and to evaluate second-order rate constants during reaction of approximately a fourth of the dialkylmercury. The stoichiometry was treated as in equation 3,

TABLE II

ACETOLYSIS OF 0.0462 *M* DIPHENYLMERCURY(I) AT 25.01°

Time, sec.	HBr,[a] ml.	[RHgOAc] *M*	10^4k_1, sec.$^{-1}$
0	1.368	0.01621	. .
190	1.600	.01896	5.07
380	1.850	.02192	5.57
705	2.135	.02530	5.13
970	2.362	.02799	5.15
1,160	2.460	.02915	4.88
1,330	2.575	.03051	4.88
1,515	2.650	.03140	4.67
1,786	2.820	.03342	4.79
1,995	2.960	.03508	4.99
2,230	3.070	.03638	4.97
70,000(∞)	3.895	.04616	——
		Mean	4.98 ± 0.18

[a] Volume of 0.05122 *M* hydrogen bromide per 4.321-ml. aliquot.

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(7) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 132 (1928).

(8) N. Muller, L. W. Pickett and R. S. Mulliken, THIS JOURNAL, **76**, 4770 (1954).

(9) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

(10) See H. G. Kuivila and A. R. Hendrickson, *ibid.*, **74**, 5068 (1952), and C. Eaborn, *J. Chem. Soc.*, 3148 (1953), for similar work on electrophilic substitution of benzeneboronic acids and arylsilanes, respectively.

TABLE III

ACETOLYSIS OF 0.05442 *M* DI-*n*-BUTYLMERCURY AT 50.06°

Time, sec.	[RHgOA *M*	$10^5 k_1$, sec.$^{-1}$
0	0.00122	..
1220	.00358	3.77
2440	.00592	3.84
4380	.00911	3.72
7630	.01422	3.73
11580	.01962	3.73
15000	.02397	3.79
20580	.02935	3.73
28080	.03529	3.73
∞	.05371[a]	——
	Mean	3.76 ± 0.04

[a] Used as initial concn. of R_2Hg.

and second-order rate constants were evaluated

$$RHgR + HClO_4 \longrightarrow RHgClO_4 + RH \qquad (3)$$

using the integrated form of equation 4. A run employing 0.022 *M* perchloric acid at 49.62° is illustrated in Table IV. Table V, which sum-

$$-d[R_2Hg]/dt = k_2[HClO_4][R_2Hg] \qquad (4)$$

marizes all the solvolyses, shows that the second-order constants agree over a twofold change in concentration of each reactant. Thus the cleavage is first order in strong acid and first order in mercurial.

TABLE IV

SOLVOLYSIS OF 0.06298 *M* DINEOPHYLMERCURY(IV) AT 49.62° WITH 0.02237 *M* PERCHLORIC ACID IN ACETIC ACID

Time, sec.	$[R_2Hg]$, *M*	$[HClO_4]$, *M*	10^3k_2, l. mole^{-1} sec.$^{-1}$
0	0.06122	0.02061	..
375	.05829	.01768	7.1
780	.05556	.01495	6.8
1185	.05353	.01292	6.9
1540	.05168	.01107	7.2
1890	.05047	.00986	7.1
4405	.04480	.00419	7.2
		Mean	7.0 ± 0.1

Discussion

Mechanism.—The present study has disclosed both a neutral first- and an acidic second-order acetolysis of typical dialkylmercury compounds, and it is interesting to assess their relative importance. The ratio of second-order to first-order rate constants for dineophylmercury (IV) at 50° is 10^4. Thus, even at 10^{-2} *M* perchloric acid, the second-order reaction is 100 times as important as the first-order one.

In considering possible mechanisms for the acetolysis one needs to recognize that nucleophilic attack on mercury[6] may contribute along with electrophilic attack on carbon to the determination of rate. In Table VI are listed some possible combinations of electrophilic and nucleophilic species for solvolysis of a carbon–mercury bond in acetic acid solvent. These combinations are classified under basic, neutral or acidic acetolysis, and along side each combination is given the apparent kinetic order of the reaction.

The absence of an appreciable effect of added acetate ion on rate of acetolysis helps to rule out some of the possible mechanisms. There would appear to be no appreciable basic acetolysis. Also, for the neutral acetolysis, the combination of AcOH as the electrophilic reagent and AcOH as the nucleophilic reagent seems unlikely, for, on that basis, the AcOH, $\overset{\ominus}{\text{OAc}}$ combination would be expected to give a much larger rate. The possibility that neutral acetolysis is actually simple acid catalysis, caused only by the action of $\overset{\oplus}{\text{AcOH}_2}$ maintained at constant concentration by autoprotolysis of the acetic acid solvent, may also be ruled out. The addition of base would be expected to produce an enormous decrease in rate, an effect which is not observed.

Of the remaining possible mechanisms for the

TABLE V

SUMMARY OF SOLVOLYSIS RATES

Temp., °C.	Concn. 10^2 *M*	*k*, sec.$^{-1}$	ΔH ≠, kcal./mole	ΔS ≠, e.u.
		$(C_6H_5)_2Hg$		
25.01	4.62	$(4.98 \pm 0.18) \times 10^{-4}$		
25.01	4.81	$(5.30 \pm 0.23) \times 10^{-4}$		
		$(s\text{-}C_4H_9)_2Hg$		
25.00	5.70	$(2.20 \pm 0.30) \times 10^{-5}$		
25.00	5.27	$(2.40 \pm 0.15) \times 10^{-5}$		
50.01	5.27	$(1.56 \pm 0.09) \times 10^{-4}$		
50.01	5.70	$(1.38 \pm 0.10) \times 10^{-4}$		
		$(n\text{-}C_4H_9)_2Hg$		
25.0[a]		2.4×10^{-6}	20.4	−16
50.06	5.70	$(3.77 \pm 0.06) \times 10^{-5}$		
50.06	5.44	$(3.76 \pm 0.04) \times 10^{-5}$		
75.05	5.70	$(3.92 \pm 0.12) \times 10^{-4}$		
75.05	5.44	$(3.90 \pm 0.18) \times 10^{-4}$		
		(Neophyl)$_2$Hg		
25.0[a]		3.6×10^{-8}	22.6	−17
50.0[a]		7.3×10^{-7}		
75.10	9.70	$(1.02 \pm 0.02) \times 10^{-5}$		
75.04	8.49	$(1.02 \pm 0.005) \times 10^{-5}$		
99.61	4.95	$(9.44 \pm 0.14) \times 10^{-5}$		
99.61	5.93	$(9.26 \pm 0.14) \times 10^{-5}$		
74.97	5.13[c]	$(0.95 \pm 0.04) \times 10^{-5}$		
49.62	6.30[d]	$(7.0 \pm 0.1) \times 10^{-3}$[b]		
49.62	3.12[e]	$(6.7 \pm 0.7) \times 10^{-3}$[b]		

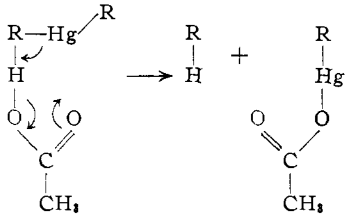
[a] Calculated from data at the other temperatures. [b] Second-order constant, l. mole^{-1} sec.$^{-1}$. [c] Other solute 0.0492 *M* NaOAc. [d] Other solute 0.02237 *M* $HClO_4$. [e] Other solute 0.04474 *M* $HClO_4$.

TABLE VI

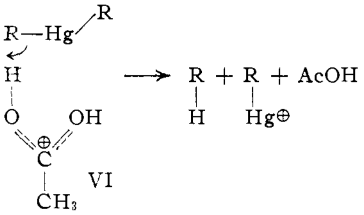
POSSIBLE COMBINATIONS OF ELECTROPHILIC AND NUCLEOPHILIC REAGENTS IN ACETOLYSIS OF DIALKYLMERCURY

Acetolysis	Reagents	Order	Possible mechanism
Basic	AcOH, $\overset{\ominus}{\text{OAc}}$	2	S_E2
Neutral	AcOH, AcOH	1	S_E2
	$\overset{\oplus}{\text{AcOH}_2}$, $\overset{\ominus}{\text{OAc}}$	1	S_E2
	AcOH	1	S_E2, S_Ei
Acidic	$\overset{\oplus}{\text{AcOH}_2}$	2	S_E2, S_Ei
	$\overset{\oplus}{\text{AcOH}_2}$, AcOH	2	S_E2, S_Ei

neutral acetolysis, one involves the combination, $\overset{\oplus}{\mathrm{AcOH_2}}$ and $\overset{\ominus}{\mathrm{OAc}}$, resulting from autoprotolysis, and the other involves AcOH. The former, while not rigorously disproved by the present data, is made somewhat unlikely by what must be an extremely low autoprotolysis for an acid solvent such as acetic acid with such a low dielectric constant (*ca.* 6). The latter seems to us the more likely, an S_Ei mechanism, as depicted in V, similar to the one suggested by Johnson[11] for hydrogen chloride cleavage, being the most attractive. This mechanism is probably also analogous to that of the iodine–iodide ion cleavage.[6]


V

For the second-order acidic solvolysis involving strong acid, an S_E2 mechanism, as in VI, seems a likely possibility. However, a solution of $\mathrm{R\overset{\oplus}{Hg}}$ in acetic acid tends to be somewhat acidic,[6,12] indicating considerable conversion to RHgOAc. This suggests the possibility of assistance from nucleophilic attack on mercury even in the acidic solvolysis of dialkylmercury. Thus possible alternative mechanisms for the acidic solvolysis involve the S_Ei type involving $\overset{\oplus}{\mathrm{AcOH_2}}$, and the S_E2 or S_Ei type involving $\overset{\oplus}{\mathrm{AcOH_2}}$ and an additional molecule of acetic acid.


VI

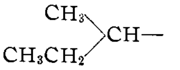
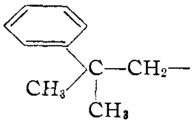
While the acidic solvolysis involving perchloric acid in glacial acetic acid has been discussed in terms of the action of $\overset{\oplus}{\mathrm{AcOH_2}}$, it is clear that perchloric acid is completely ionized but only very slightly dissociated.[13] Therefore, ion pairs, $\mathrm{Ac\overset{\oplus}{O}H_2\overset{\ominus}{Cl}O_4}$ and $\mathrm{RH\overset{\oplus}{g}\overset{\ominus}{Cl}O_4}$, perhaps both intimate and solvent-separated,[14] should be employed in the interpretation of the kinetics. However, the implications of ion pair considerations have not been explored.

Reactivity.—The observed rate constant for neutral acetolysis of diphenylmercury(I) in the present work was similar in magnitude to the value reported by Corwin and Naylor[5] in 50% AcOH–dioxane. The present value in pure acetic acid at 25°, 5×10^{-4} sec.$^{-1}$, is nearly exactly equal to the reported value in 50% AcOH–dioxane at 42°.

As expected, the rate of acetolysis of diphenylmercury(I) exceeds very substantially that of the aliphatic dialkylmercuries. The relative rates of acetolysis of the four dialkylmercuries are summarized in Table VII, along with two other sets of relative rates in other electrophilic substitutions of organomercurials. The sequence, $(C_6H_5)_2Hg$ > $(s\text{-Bu})_2Hg$ > $(n\text{-Bu})_2Hg$ > $(\text{neophyl})_2Hg$, observed in neutral acetolysis, is the same as the one observed in triiodide ion cleavage of alkylmercuric iodides,[6] although the gap between phenyl and *s*-Bu in the latter case is considerably larger. The portion of the rate sequence, *s*-Bu > *n*-Bu, also is observed in the rough rates of butane evolution reported by Marvel and Calvery[15] for the action of concentrated hydrochloric acid on the dibutylmercury compounds. For this heterogeneous reaction, relative rates were reported: *t*-Bu, 6 > *s*-Bu, 2 > *n*-Bu, 1.

TABLE VII

RELATIVE RATES OF ELECTROPHILIC SUBSTITUTION

R	Rel. rate R_2Hg + AcOH, 25°	log	Rel. rate[6a] RHgI + $I_3^{\ominus}$, 25°	log	Rel. rate[15] R_2Hg + HCl, 26°
	14,000	4.15	134,000	5.13	
 $(CH_3)(CH_3CH_2)CH-$	640	2.81	807	2.91	2[b]
$CH_3CH_2CH_2CH_2-$	65	1.81	115	2.06	1
	1	0	1[a]	0	

[a] Extrapolated from data at higher temperatures.[6] [b] *t*-Bu, 6.

Broadly generalizing, one can anticipate that rates of electrophilic substitution on carbon will fall off as the attack is on: (i) a lone pair, (ii) an aromatic or vinyl carbon atom, or (iii) a saturated carbon atom Considering the transition state VII for electrophilic substitution on RX by E, the usual superiority of aryl lies in the contribution of structure VIIb, aryl being a source of originally π-electrons.[16]

The prediction of the rate sequence among aliphatic R groups is as difficult as for nucleophilic substitution.[17] The effect of variation in R on rate will depend on the importance of bond making and breaking (VIIcd). Another consideration is possible bonding[2] between X and E with consequent

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[11] J. R. Johnson, Chapter 25 in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943.

[12] See also F. H. Westheimer, p. 13 of Abstracts of Eleventh National Organic Chemistry Symposium, Madison, Wis., June 20–22, 1949, for mercuric ion in acetic acid.

[13] T. Smith and J. H. Elliot, THIS JOURNAL, **75**, 3566 (1953).

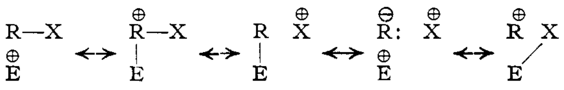
[14] S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *ibid.*, **76**, 2597 (1954); *Chemistry & Industry*, 664 (1954).

[15] C. S. Marvel and H. O. Calvery, THIS JOURNAL, **45**, 820 (1923).

[16] This is important whether or not a benzenium ion intermediate II intervenes. None of the evidence on the neutral acetolysis of diphenylmercury(I) either demands or disproves the intervention of such an intermediate.

[17] *E.g.*, S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

cationic character[18] in R (VIIe). Not indicated in VII is possible nucleophilic attack on X involved in S_E2 or S_Ei mechanisms, which would affect the response of rate of electrophilic substitution on R



VIIa b c d e

to change in R. The effects of substituents on X are especially serious. For example, rates of electrophilic substitution on R are enormously greater for X = HgR than for X = HgCl. Steric considerations are also important.

The rate sequence *s*-Bu > *n*-Bu in the three cases summarized in Table VII is the one predicted by Hughes and Ingold.[19] However, the rate factors are small, being 2, 7, and 10. Further, this rate sequence is actually the reverse of the order *n*-Bu > *s*-Bu, reported[4] for the preferred site of electrophilic displacement in the hydrogen chloride cleavage of unsymmetrical dialkylmercury compounds. Thus no uniform large difference in relative rates of electrophilic substitution on *s*-Bu and *n*-Bu is in evidence. More extensive experimental material dealing with relative rates of electrophilic substitution on aliphatic carbon will be presented and discussed in a subsequent article.

Experimental Part

All melting points are corrected.

Diphenylmercury.—This material, m.p. 124.5–125.0°, was prepared by the method of Maynard.[20]

Di-*s*-butylmercury.—A solution of 113 g. (0.5 mole) of stannous chloride dihydrate in 600 ml. of water was placed in a 2-liter round-bottom flask. Sodium hydroxide (6 *N*) was added to this solution until the precipitate which first formed, just dissolved. To this solution was added 77 g. (0.2 mole) of *s*-butylmercuric iodide.[6a] The reaction mixture was shaken for two days, and the resulting gray suspension was extracted with about 50 ml. of redistilled Skellysolve B. The extract was dried over potassium carbonate, and the low boiling solvent was distilled off at atmospheric pressure. The remaining liquid was distilled through a center-rod column to yield 16.2 g. of material, b.p. 95.5–97.0° (18 mm.), n^{25}_D 1.5110. All the fractions developed metallic mercury on standing a few hours. These fractions were combined and redistilled through the center-rod column at 1.3 mm. pressure, the major portion distilling at 44.5°; reported properties[15,21] b.p. 93–96° (18 mm.), n^{20}_D 1.511, b.p. 51–54° (2 mm.).

Di-*n*-butylmercury.—Redistilled Eastman Kodak white label material, b.p. 91–93° (6 mm.), was employed.

Dineophylmercury.—The first preparation of this material was carried out by Lee Kent. To a filtered solution of neophylmagnesium chloride prepared from 12.2 g. of magnesium and 84 g. (0.5 mole) of neophyl chloride was added 75 g. (0.2 mole) of neophylmercuric chloride.[6a] The reaction was not exothermic, but the mixture became an opaque white suspension in half an hour. After the mixture stood at room temperature for 48 hours, it was cooled and hydrolyzed with ice-water and then acetic acid. The ether layer was separated, washed with water, dried, and then concentrated at reduced pressure. The residual oil was placed under 10^{-5} mm. for two days, and then the clear tan residual oil was crystallized from methanol–ether at Dry Ice temperature to yield 60 g. of fine white needles, m.p. 26.0–26.5°.

Anal. Calcd. for $C_{20}H_{26}Hg$: C, 51.43; H, 5.61. Found: C, 51.49; H, 5.70.

A solution of 0.9011 g. of dineophylmercury and 0.524 g. of mercuric chloride in 20 ml. of ether was left at room temperature for two days. Evaporation of the ether and recrystallization of the residue from methanol yielded 1.199 g. (84%) of neophylmercuric chloride, m.p. 80.3–81.5°, mixed m.p. with authentic material (80.6–81.3°) being 80.3–81.5°.

Dineophylmercury also was prepared from neophylmercuric chloride by the method described above for di-*s*-butylmercury, except that the product was isolated by recrystallization from absolute ethanol at −80°. The yield of material, m.p. 24.5–24.8° (uncor.) undepressed by the material prepared by the Grignard method, was 85%.

Rates of Solvolysis.—The solvent was Baker and Adamson glacial acetic acid, dried by the acetyl borate method of La Mer and Eichelberger.[22] Karl Fischer titration indicated 0.006% water.

Microburets of 5-ml. volume were used without calibration. The automatic pipet was calibrated with acetic acid to a reproducibility within 0.1%.

Standard hydrogen bromide solution, used in the titration of rate aliquots, was made up by adding dry acetic acid to the proper amount of 48% aqueous hydrobromic acid. It was standardized against sodium acetate in acetic acid each day of use.

For following the solvolysis, the dialkylmercury compound was dissolved in acetic acid, and aliquots were sealed in ampules (when time permitted) and placed in a constant temperature oil-bath at the proper temperature. One minute was allowed for the solution to come to temperature. Ampules were removed, quenched in a water-bath at 25°, broken, and 4.321-ml. aliquots removed with an automatic pipet. The aliquots were titrated with hydrobromic acid in acetic acid to a brom phenol blue end-point.[6a] There was no end-point drift in the infinity titers. The aliquots which contained dialkylmercury gave fading end-points. Addition of hydroquinone to the titration solution stabilized end-points for about 30 to 50 seconds for dineophyl- and di-*n*-butylmercury. With diphenylmercury and di-*s*-butylmercury, the end-points still drifted too rapidly for very accurate titrations. In these two cases it was advantageous to overtitrate about 0.04 ml., in which case the indicator color returned after *ca.* 15 seconds. With this method, it was possible to obtain rate constants sufficiently accurate for comparisons of relative rate.

In the solvolysis of dineophylmercury in the presence of perchloric acid, the mercurial was dissolved in the perchloric acid solution and made up to volume with this solution. Aliquots (4.321 ml.) were withdrawn at intervals, drained into 4.321 ml. of 0.04747 *N* sodium acetate in acetic acid, and back titrated with 0.05000 *N* hydrobromic acid.

Diphenylmercury solvolyzed very rapidly in acetic acid, while the rate of solution was quite low. For this reason about 1.5 times the amount needed was placed in 50 ml. of the solvent and shaken for approximately one minute; then the solution was filtered into a flask in the 25° thermostat. Aliquots were withdrawn and titrated immediately in the presence of hydroquinone, the times being taken at the end of each titration.

Solvolysis Products. Diphenylmercury.—This compound (7.04 g., 0.0198 mole) was dissolved in 100 ml. of glacial acetic acid and left at 25° for 12 hours (30 half-lives). The solution was evaporated to dryness and the resulting white solid dried over sodium hydroxide pellets overnight. There was obtained 6.9 g. (88.3%) of material, m.p. 146.2–148.7°, m.p. 150.6–151.3° after recrystallization. In previous work in these laboratories, Keller[6a] observed m.p. 149.5–151.0° for phenylmercuric acetate.

Di-*n*-butylmercury.—This compound (9.9 g., 0.0314 mole) was dissolved in 100 ml. of glacial acetic acid and kept at 75° for 6 hours (11 half-lives). About 5 g. of lithium chloride in 20 ml. of glacial acetic acid was added to the solvolysis solution, which was then cooled to 25°. The butylmercuric chloride crystallized out. The precipitation was

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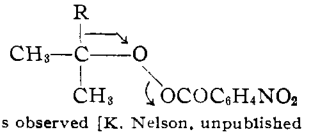
[18] This consideration appears to be extremely important in certain rearrangement reactions. For example, in ionization of α-alkylisopropyl per-*p*-nitrobenzoates, a very steep rate sequence, *t*-Bu > *i*-Pr > Et > Me, is observed [K. Nelson, unpublished work].



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completed by adding water, and the solid was filtered off and dried over phosphorus pentoxide to yield 8.6 g. (94%) of material, m.p. 126.8–127.8°, m.p. 126.9–127.5° after recrystallization. Keller[6a] observed m.p. 128.3–128.8° for *n*-butylmercuric chloride.

Dineophylmercury.—Dineophylmercury (5.5 g., 0.0118 mole) was dissolved in 65 ml. of glacial acetic acid and this solution was sealed in a 100-ml. ampule. After 40 hr. at 100° (20 half-lives), the ampule was opened and the solution was decanted from 0.160 g. (0.0008 mole) of metallic mercury. Aqueous lithium chloride was added to the solution to precipitate neophylmercuric chloride which was filtered off, washed with water and air-dried. The crude yield was 3.9 g. (89%), m.p. 70–79°, m.p. 79.5–80.5° after one recrystallization from ethyl acetate–Skellysolve B. Keller[6a] observed 79.2–79.5° and Kent[23] 80.6–81.2° for the m.p. of neophylmercuric chloride.

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[23] L. Kent, unpublished work.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Base Strengths and Ultraviolet Absorption Spectra of the 2- and 3-Monohalopyridines[1,2]

BY HERBERT C. BROWN AND DARL H. MCDANIEL[3]

RECEIVED SEPTEMBER 27, 1954

Ultraviolet absorption spectra have been determined for the 2- and 3-monohalopyridines in basic and acidic aqueous solution. The spectra exhibit a regularity which is absent in the corresponding monohalonitrobenzenes. The data have been utilized to determine the dissociation constants for these pyridine bases. The following thermodynamic pK_a values at 25° have been observed: 2-fluoro-, −0.44; 2-chloro-, 0.72; 2-bromo-, 0.90; 2-iodo-, 1.82; 3-fluoro-, 2.97; 3-chloro-, 2.84; 3-bromo-, 2.84; 3-iodo-, 3.25. Thus the introduction of a fluorine atom in the 2-position of the pyridine ring results in an enormous decrease of 5.6 pK_a units. The remaining halogens are somewhat less effective in decreasing the base strength and the magnitude of the effect decreases with increasing atomic weight of the halogen. In the 3-position the effect is less marked. There is a decrease of approximately 2 pK_a units with no simple regularity in the pK_a values.

In a previous paper the dissociation constants of pyridine, 2,6-lutidine and thirteen monoalkylpyridines were reported.[4] It was considered desirable to extend the series of measured dissociation constants to include pyridine bases with more highly polar substituents. Therefore, the dissociation constants were measured for the 2- and 3-moonhalopyridines. The 4-halopyridines were not included in this investigation because of the reported instability of some of these compounds.[5]

The pK_a values of the pyridine bases were determined by utilizing ultraviolet absorption spectra to measure the concentration of the free and protonated pyridine bases in solutions of measured pH.[4,6] The method required the determination of the ultraviolet absorption spectra of both the free and protonated form of each of the monohalopyridines. These spectra reveal interesting similarities and differences with the corresponding spectra of the monohalonitrobenzenes.[7] Accordingly, consideration of the spectra appears of interest.

Results and Discussion

Dissociation Constants.—The pK_a values obtained for the 2- and 3-monohalopyridines are summarized in Table I. The error given represents the precision of the results, not the accuracy. It is probable that the error in terms of accuracy is greater than the error in precision by at least 0.02 pK_a unit.

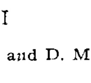
In the case of 2-fluoropyridine it was necessary to make certain assumptions in correcting the spectral data, assumptions that might result in a considerable error. Moreover, the common practice was followed of not correcting for the activity coefficient of the neutral species in rather strong acid solutions. The recent work of Long and McIntyre[8] indicates that such activity coefficients may vary appreciably from unity. Thus the error in the case of 2-fluoropyridine may be considerably larger than in the other case, possibly as large as ±0.3 pK_a unit.

TABLE I

THERMODYNAMIC pK_a VALUES FOR THE 2- AND 3-MONOHALOPYRIDINES IN AQUEOUS SOLUTION AT 25°

Compound	pKa
Pyridine[4]	5.17 ± 0.02
2-Fluoropyridine	−0.44 ± .08
2-Chloropyridine	+ .72 ± .03
2-Bromopyridine	.90 ± .05
2-Iodopyridine	1.82 ± .02
3-Fluoropyridine	2.97 ± .05
3-Chloropyridine	2.84 ± .03
3-Bromopyridine	2.84 ± .03
3-Iodopyridine	3.25 ± .05

The introduction of a fluorine atom in the 2-position of the pyridine base results in the surprisingly large decrease in pK_a value of 5.6 units. This large decrease is unexpected since fluorine is believed to participate in resonance interactions I which should tend to decrease the inductive effect of the substituent II. It must be concluded that in this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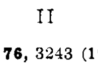
II

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[1] Steric Effects in Displacement Reactions. VII.

[2] Based upon a thesis submitted by Darl H. McDaniel in August, 1954, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Research assistant at Purdue University, 1952–1953, on a National Science Foundation grant; Allied Chemical and Dye Corporation Fellow at Purdue University, 1953–1954.

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