

**Dipole Moments.** The dipole moments of the various compounds were determined at 25° in benzene solution using the dipole moment apparatus described previously.<sup>28</sup> The moments were calculated essentially by the method of Halverstadt and Kumler,<sup>29</sup> utilizing an IBM 7070 computer as described earlier.<sup>30</sup> The

(28) N. L. Allinger, H. M. Blatter, M. A. DaRooge, and L. A. Friberg, *J. Org. Chem.*, **26**, 2550 (1961).

(29) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(30) N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

molar refractivities were obtained from tables,<sup>21</sup> and atomic polarization was neglected. The data are summarized in Table I.

**Acknowledgment.** After this paper was written we learned from Professor A. R. Katritzky that studies in his laboratory along similar lines had been made by his group.<sup>31</sup> Our results and conclusions are in good agreement. We are indebted to Professor Katritzky for this information prior to publication.

(31) A. R. Katritzky, *Proc. Chem. Soc.*, in press.

## A Kinetic and Mechanistic Study on the Cleavage of the Carbon–Boron Bond. The Importance of Coordination

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The mechanism of the reaction of triethylboron with carboxylic acids has been examined kinetically in aprotic solvents. The reaction is first order in each reagent, and  $\log k_2$  is an inverse function of the  $pK_a$  of the acid. A Taft correlation ( $\rho^* = -0.94$ ) is observed. The effect of added nucleophiles and a primary isotope effect ( $k_{RCOOH}/k_{RCOOD} = 3.3$ ) indicate that pre-rate-determining nucleophilic coordination of the organoborane by the oxy functions of the acid occurs, a step which activates both the incipient carbanion and the electrophilic hydrogen of the acid.

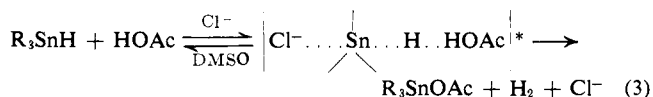
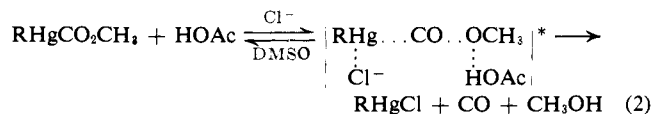
During the last decade considerable attention has been paid to the detailed mechanistic processes involved in the cleavage of carbon–metal bonds, particularly by protic acids, a process fundamental to an understanding of organometallic chemistry in general.

There is considerable qualitative evidence for nucleophilic participation<sup>2</sup> at metal in addition to the electrophilic attack at adjacent carbon.



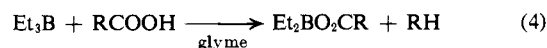
The nucleophile may be an independent species, solvent, or incorporated in an electrophile–nucleophile pair.

In order to elaborate further on the details of this type of process, and to demonstrate the validity of the concept across the periodic table, two previous studies<sup>3</sup> have explored kinetically the cases where the central metal ion was  $d^{10}$  (mercury) and  $d^0$  (tin) as in eq. 2 and 3. It was concluded that the function of the



added halide ion was to coordinate with the metal, thus weakening the metal–carbon (or hydrogen) linkage, and serve as an assistor for the subsequent, and rate-determining, proton attack. It was pointed out that this type of nucleophilic catalysis was solvent dependent, and was not observed in the tin system if a protic environment was used,<sup>4</sup> one in which nucleophilic activity of added anions was diminished by hydrogen bonding.

The present paper reports on the last of this series, one in which the cleavage of carbon–boron bonds is studied. This involves what might be termed as a “no d” case, since no low-lying d-orbitals are available to boron, although an open p is. In particular, the reaction



has been examined. The published evidence records the fact that although carboxylic acids cleave the C–B bond readily, hydrohalic acids are relatively inefficient.<sup>5</sup> Recognizing the incompatible hard–soft properties of boron and chloride ion,<sup>6</sup> the hypothesis that nucleophilic attack at boron, as well as electrophilic attack at carbon, were important in determining the height of the tran-

(4) H. Kuivila, personal communication.

(5) (a) J. Goubeau, R. Epple, D. D. Ulmschneider, and H. Lehmann, *Angew. Chem.*, **67**, 710 (1955); (b) H. Meerwein, G. Hinz, H. Majert, and H. Sönke, *J. prakt. Chem.*, **147**, 226 (1936); (c) H. C. Brown and K. J. Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959); (d) H. C. Brown, “Hydroboration,” W. A. Benjamin, Inc., New York, N. Y., 1962, p. 65.

(6) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(1) Alfred P. Sloan Foundation Fellowship.

(2) See Discussion.

(3) (a) R. E. Dessy and T. Hieber, *J. Am. Chem. Soc.*, **86**, 28 (1964);

(b) R. E. Dessy and F. E. Paulik, *ibid.*, **85**, 1812 (1963).

sition state barrier would well explain this observation. Brown, without data,<sup>6d</sup> has written a proposed mechanism for the carboxylic acid cleavage, and the following data will end by supporting this proposal.

### Experimental

**Apparatus and Starting Materials.** The Thomas Van Slyke manometric apparatus was used. The liquid acids were purified by distillation and the solid ones by recrystallization. All acids were commercial preparations. Triethylboron was obtained from Stauffer Chemical Co., Anderson Chemical Division. Vapor phase chromatography indicated one major and a trace of two minor components. Bulb-to-bulb distillation of a high-vacuum line gave a material which when analyzed by v.p.c. gave the same two minor components. Therefore, it was concluded that there was slight cracking of the triethylboron occurring on the column. Thus, the triethylboron was used as obtained. The diglyme solvent, "Ansul 141," was purified by refluxing over sodium metal for several days followed by distillation under a nitrogen atmosphere. The deuterated acetic acid was prepared by the method of Roberts, *et al.*<sup>7</sup>

**Typical Procedure for the Preparation of Triethylboron Standard Solution.** Since ethane was soluble in diglyme and acetic acid, it was necessary to prepare two solubility graphs, one for a 50-50 mixture of diglyme and acetic acid (ethane solubility is 25%) and the other for pure diglyme (ethane solubility is 30%). This was accomplished by evacuating the reaction vessel and injecting 20 ml. of diglyme (or 10 ml. of acetic acid) by the use of a syringe. After stirring for several minutes at constant temperature (31°) the stirring was stopped and ethane gas was slowly added to a known pressure. When the stirring was started, the decrease in pressure that occurred was measured. This procedure was repeated several times at varying initial pressures. Thus, a plot of equivalent millimeters of gas in solution vs. observed pressure was constructed.

A triethylboron solution containing (1.8 g., 0.0183 mole) triethylboron in 100 ml. of diglyme was prepared. The reaction vessel of the Van Slyke instrument was evacuated and 10 ml. of the triethylboron solution was added by the use of a syringe. After stirring for several minutes at constant temperature (31°), 10 ml. of anhydrous acetic acid was added. Gas evolution was quite rapid and a constant reading was obtained within 30 min. as indicated by the data in Table I. To the total pressure change, 23.3

Table I

Time, min.	Pressure, cm.	Time, min.	Pressure, cm.
0.0	16.70	12	39.95
1	32.80	20	39.95
2	38.60	33	40.0
5	39.90	75	40.0

cm., the following corrections were made: (+1.4 cm.) the vapor pressure change due to triethylboron

(7) J. D. Roberts, C. M. Regan, and I. Allen, *J. Am. Chem. Soc.*, 74 3679 (1952).

Table II<sup>a</sup>

Pressure, cm.	Time, min.	$\Delta P$	$\Delta P^b$	$a - x^c$	$\frac{1}{a - x} \times 10^2$
17.5	0	0	0	35.9	2.79
19.2	3	1.7	2.3	33.6	2.98
21.4	7	3.9	5.5	30.4	3.29
23.2	11	5.7	8.1	27.8	3.60
24.7	15	7.2	10.2	25.7	3.89
26.4	20	8.9	12.6	23.3	4.28
28.2	27	10.7	15.2	20.7	4.83
30.5	38	13.0	18.4	17.5	5.72
32.2	50	14.7	20.9	15.0	6.67
33.4	60	15.9	22.6	13.3	7.52
34.4	70	16.9	24.0	11.9	8.41
35.8	90	18.3	26.0	9.9	10.10
36.8	110	19.3	27.4	8.5	11.75
37.2	120	19.7	28.0	7.9	12.65
41.4	19 (hr.)	23.9	34.1		

<sup>a</sup> Plotting the reciprocal of concentration vs. time gives a rate constant ( $k$ ) of  $4.7 \times 10^{-3} M^{-1} \text{ sec.}^{-1}$ . Conditions: evacuated flask at 14.5 cm., 10-ml. solution of  $\text{Et}_3\text{B}$  at 16.7 cm., and 10-ml. solution of acetic acid at 17.5 cm. (15 sec.). <sup>b</sup> Corrected for ethane solubility. <sup>c</sup>  $a$  = initial concentration of reactants expressed in volume,  $x$  is volume of ethane evolved.

Table III

$(\text{C}_2\text{H}_5)_3\text{B} + \text{RCOOH} \xrightarrow[31^\circ]{\text{diglyme}} \text{C}_2\text{H}_6 + (\text{C}_2\text{H}_5)_2\text{BO}_2\text{CR}$			
RCOOH	Acid concn.	Boron concn.	$k_2$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
$\text{CH}_3\text{COOH}$	0.10	0.10	$4.7 \times 10^{-3}$
	0.21	0.10	$4.1 \times 10^{-3}$
	0.05	0.10	$5.1 \times 10^{-3}$
$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	0.10	0.10	$5.9 \times 10^{-3}$
	0.05	0.10	$5.3 \times 10^{-3}$
	0.20	0.10	$5.6 \times 10^{-3}$

(determined by the pressure difference between 10 ml. of pure diglyme and 10 ml. of triethylboron solution); (-2.1 cm.) the pressure change due to the addition of 10 ml. of acetic acid; and (+7.4 cm.) the solubility of ethane in a 50-50 mixture of diglyme and acetic acid. Therefore, the total amount of gas evolved gave rise to a pressure change of 30 cm. The calculated pressure change was 30.5 cm. Thus, greater than 98% of theory of triethylboron was accounted for.

**Typical Reaction of Triethylboron and an Acid.** Into the evacuated flask of the Van Slyke instrument was placed 10 ml. of a 0.21  $M$  solution of triethylboron. After stirring for several minutes at a constant temperature (31°) 10 ml. of a 0.21  $M$  solution of acetic acid was added. The data in Table II were obtained.

### Results and Discussion

The reaction of triethylboron with a series of substituted acetic and benzoic acids in diglyme was studied kinetically by a manometric method which followed the rate of evolution of ethane. Variation in the initial concentrations of the reactants, as well as application of tests by kinetic equations within a run, indicated that the process, for the triethylboron, octanoic and acetic acid pairs, was first order in each component. Some deviation of calculated rate constants was found, but these involve large changes in solvent pool charac-

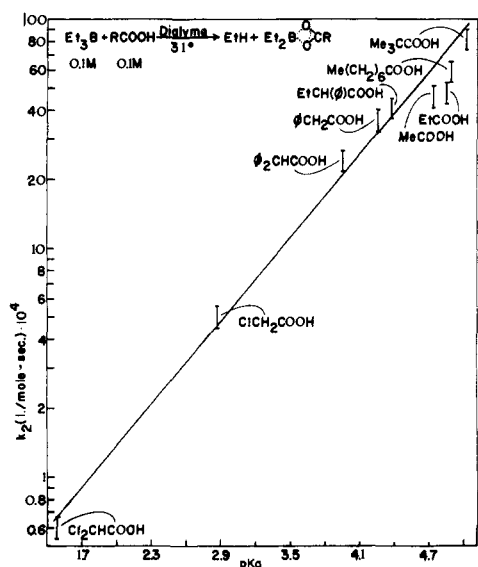


Figure 1.

teristics, both at the start of the run and during it (see Table III).

Duplicate kinetics runs employing other acids at equimolar initial concentrations were run, and the results are shown in Figure 1 (Table IV). Molecular weight measurements assured the absence of polymeric species for products or reactants, except in the case of acetic, pivalic, and propionic acids.<sup>8</sup> These points still fit the correlation observed for the other acids, suggesting that if association is present it does not interfere with the main course of the reaction. Figure 1 provides a plot of  $\log k_2$ , the second-order rate constant for the cleavage reaction, vs. the reported  $pK_a$  value<sup>9</sup> of the acids in water. The actual  $pK_a$  values for acids in water will be changed in transferring to diglyme, but the sequence should not. Thus, the comparison seems a fair one.

A linear relationship is noted between the  $\log k_2$  and  $pK_a$  for both series of acids. In particular the substituted acetic acids involve a span of  $-2.2$  log units in rate and  $3.6$  log units in  $K_a$  with a slope of  $0.6$ . Also the Taft relationship,  $\log k/k_0 = \sigma^* \rho^*$ , correlates the data ( $r = 0.98$ ) yielding a  $\rho^* = -0.94$ . The benzoic acid sequence, although a more limited extent, possesses a slope of  $1$ . Since only a limited number of runs was obtained, it was felt that it did not warrant graphical presentation. The data are found in Table IV. The important observation is that the stronger the acid, the slower the rate of cleavage.


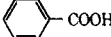
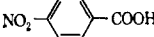





Although such a limited selection of data does not exclusively point to a unique mechanism for the process, they do eliminate several obvious possibilities.

The reactions of  $BH_4^-$  with protic acids such as phenol or methanol<sup>10</sup> obey a third-order rate expres-

(8) The molecular weight determinations were made using a Mechrolab osmometer Model 301. Acetic and propionic acid gave abnormal results due to high volatility. Pivalic acid and acetamide were found to be dimeric in diglyme solvent. This dimeric nature did not affect the kinetic picture.

(9) (a) "Handbook of Chemistry and Physics," 43rd Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1962; (b) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall Co., Inc., New York, N. Y., 1952, p. 556; (c) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., Ltd., London, John Wiley and Sons, Inc., New York, N. Y., 1962.

Table IV

Acid <sup>a</sup>	$k_2$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
$(CH_3)_3CCOOH$	$8.1 \times 10^{-3}$
$CH_3(CH_2)_6COOH$	$5.9 \times 10^{-3}$
$CH_3CH_2COOH$	$4.8 \times 10^{-3}$
$CH_3COOH$	$4.7 \times 10^{-3}$
$CH_3CH_2CHCOOH$	$4.1 \times 10^{-3}$
$C_6H_5$	
$C_6H_5CH_2COOH$	$3.6 \times 10^{-3}$
$(C_6H_5)_2CHCOOH$	$2.4 \times 10^{-3}$
$ClCH_2COOH$	$5.1 \times 10^{-4}$
$Cl_2CHCOOH$	$5.9 \times 10^{-5}$
$Cl_3CCOOH$	Too slow to measure but relative order
$F_3CCOOH$	
	$10.2 \times 10^{-3}$
	$4.2 \times 10^{-3}$
	$8.6 \times 10^{-4}$
	$1.0 \times 10^{-3}$
	$8.4 \times 10^{-4}$
	$1.4 \times 10^{-4}$
	$1.0 \times 10^{-4}$
	$4.6 \times 10^{-2}$

<sup>a</sup> Acid and boron concentrations were all approximately  $0.1 M$  in the reaction mixture.

sion, rate =  $k(ROH)_2(BH_4^-)$ , apparently because the attacking species is in actuality autoprotonated  $ROH_2^+$  ( $2ROH \rightleftharpoons ROH_2^+ + RO^-$ ). The present data reveal that in the reaction of carboxylic acids with triethylboron, the  $k_2$  values are consistent, within a run and between runs, with the second-order kinetics (observations which are inconsistent with  $RCO_2H_2^+$  as an attacking species).

Also eliminated is the rate-determining dissociation of the  $R_3B$ -solvent complex. This type of mechanism has been advanced by Ryschkewitsch<sup>11</sup> for the acid-catalyzed solvolysis of some pyridine-boranes.

The kinetics cannot tell us if molecular acid is involved or a sequence by which the elements of molecular acid become associated with the substrate prior to formation of the transition state. However, observations indicate that the addition of ethyl acetate to the reaction mixture does not impede the rate, while the addition of dimethyl sulfoxide, a nucleophile toward boron, does (Table V).

Also, the addition of trifluoroacetic acid to a reaction of octanoic acid and triethylboron does not affect the

(10) R. E. Dessy and E. Grannen, *J. Am. Chem. Soc.*, **83**, 3953 (1961).

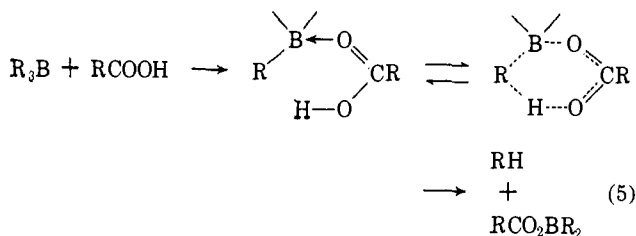
(11) (a) G. E. Ryschkewitsch, *ibid.*, **82**, 3290 (1960); (b) G. E. Ryschkewitsch and E. R. Birnbaum, *J. Phys. Chem.*, **65**, 1087 (1961); (c) G. E. Ryschkewitsch, *Advances in Chemistry Series*, No. 42, American Chemical Society, 1964, Chapter 5.

Table V

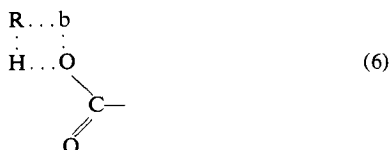
RCOOH	Acid concn.	Boron concn.	Compd. added	Concn.	$k_2$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH	0.10	0.10	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OC}_2\text{H}_5 \end{array}$	0.10	$5.6 \times 10^{-3}$
CH <sub>3</sub> COOH	0.10	0.10	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{S}-\text{CH}_3 \end{array}$	0.10	$3.1 \times 10^{-3}$
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH	0.10	0.10	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CF}_3\text{C}-\text{OH} \end{array}$	0.10	$5.8 \times 10^{-3}$

rate. Finally, alteration of the solvent from diglyme to xylene did not alter the kinetic order, but did lead to increases in observed specific rate constants. Comparisons in three specific cases (CH<sub>3</sub>COOH,  $3.8 \times 10^{-2}$ ; ClCH<sub>2</sub>COOH,  $1.3 \times 10^{-2}$ ; C<sub>6</sub>H<sub>5</sub>OH,  $4.2 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>) with the data reported in Table IV suggest that this increase is about an order of magnitude.

These factors, added to the previously mentioned observation that HCl is a poor reagent for B-C cleavage, suggests that the mechanism for the cleavage of carbon-boron bonds by carboxylic acids involves the sequence



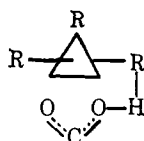
or one in which a four-center transition state<sup>12</sup> is invoked (eq. 6)<sup>13</sup>. Since the product, from infrared



spectral data, shows only one C-O absorption,<sup>16</sup> and is monomeric, suggesting a structure



it is also conceivable that pentacoordinate boron is involved in the transition state. The differentiation of



these possibilities is currently under study.

(12) R. E. Dessy and F. E. Paulik, *J. Chem. Educ.*, **40**, 185 (1963).

(13) The studies on the protonation of the carboxyl group<sup>14</sup> and amides<sup>15</sup> indicated that the carbonyl oxygen was protonated in both cases, therefore suggesting that this is the most basic site. Thus, we also prefer to favor the transition state where the carbonyl oxygen is coordinated.

(14) R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82**, 4059 (1960).

(15) G. Fraenkel and C. Franconi, *ibid.*, **82**, 4478 (1960).

(16) L. A. Duncanson, W. Gerrard, M. F. Lappert, N. Pyszora, and R. Shafferman, *J. Chem. Soc.*, 3652 (1958).

Ryschkewitsch<sup>11</sup> and Dessy<sup>12</sup> have pointed out that coordination of an organometallic compound should, in the nontransition series, make loss of an attached alkyl or hydrogen more favorable thermodynamically. This end result is often not achieved kinetically since the attacking reagent may be blocked from approach by such coordination. In the present case, assuming a similar nucleophilic character of acetic acid and ethyl acetate, and therefore the same amount of complex formation, it is obvious that an external electrophile source cannot successfully consummate the reaction. This is also shown in the trifluoroacetic acid-octanoic acid case.

It is felt that this points the way to an interpretation based not only on the effect of coordination of the oxygen of the attacking acid on the stability of the carbon-boron bond, and on its polarity, but also on the effect of the coordination on the acidity of the intramolecular proton. Coordination chemists have been familiar with this concept, noting for example the increased acidity of 4-(2-pyridylazo)resorcinol acid on coordination with metal ions.<sup>17</sup> Briefly, one may state the operational actions in the attack as involving a *coordination step that simultaneously polarizes and weakens the C-B bond, and increases the electrophilic character of the proton in question.*

Measurements of the effect of substituting CH<sub>3</sub>COOD for CH<sub>3</sub>COOH have given a  $k_{\text{H}}/k_{\text{D}}$  ratio of 3.3, compared to a  $k_{\text{H}}/k_{\text{D}}$  (max.) of 16, calculated from O-H and O-D stretching frequencies of acetic and deuterioacetic acid in diglyme (O-H = 3520 and O-D = 2333 cm.<sup>-1</sup>).<sup>18</sup> Proton transfer is involved in the rate-determining step. Thus the reaction pathway is best represented by a pre-rate-determining nucleophilic coordination step of the carboxylic acid followed by proton transfer to carbon.

One may question the label of electrophilic attack on carbon that has been often applied to this, and similar processes. In the present case, it would appear that the nucleophilic coordination step at boron was the key to the whole reaction, despite the fact that proton transfer is in whole or in part the rate-determining step.

The importance of the nucleophilic participation may be illustrated as follows. Thiophenol reacts readily with triethylboron. But phenol does not. This observation is in agreement with the report of Stone and Graham<sup>19</sup> on the relative coordinating ability of R<sub>2</sub>O

(17) A. Corsini, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **2**, 225 (1963).

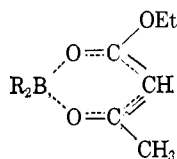
(18) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960, Chapter 2.

and  $R_2S$  toward trimethylboron. Also weak acids, such as acetamide ( $pK_a = 12.6$ ) with an internal nucleophile, capable of acidification by coordination cleave triethylboron,  $k_2 = 1.0 \times 10^{-3}$ .

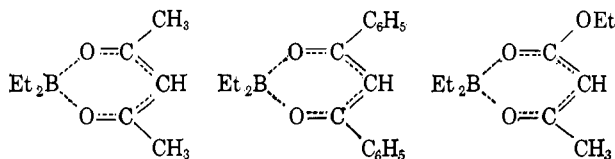
The importance of geometry in combined electrophile-nucleophile attack is also easily demonstrated. A mixture of pyridine and phenol ( $pK_a = 9.98$ ) fails to cleave the triethylboron after 7 hr., but the equally acidic 8-hydroxyquinoline<sup>9b</sup> does so readily with  $k_2 = 8.4 \times 10^{-4}$ .

Pyrrolidone and 2-pyridone ( $pK_a = 11.62$ ),<sup>20</sup> compounds that are structurally related to 8-hydroxyquinoline and acetamide, react readily with kinetics which are identical with that of the carboxylic acid case. However, it is germane to note that 4-pyridone ( $pK_a = 11.09$ )<sup>20</sup> is unreactive toward triethylboron, thus supporting the concept that it is the available nucleophile-electrophile pair in the proper geometry that is important in determining the rate, not primarily acidity.

The synthesis of compounds of the type<sup>21</sup> shown be-



low has been achieved by the reaction of  $R_2BCl$  with the  $\beta$ -keto ester, but direct reaction of  $R_3B$  with 1,3-diketones will yield similar materials readily,<sup>22</sup> as we have confirmed. The following materials have been prepared by this route, and will be reported on. These



also exemplify the fact that an intramolecular electrophile-nucleophile pair, in which coordination of the nucleophile to boron can activate the electrophile, as well as weakening the B-C bonds, leads to a very rapid cleavage.

In review then, kinetic evidence exists for three cases of pre-rate-determining coordination of nucleophile at metal in reactions involving subsequent electrophilic attack at adjacent carbon.

Kreevoy<sup>23</sup> has recently summed up his observations on the deoxymercuration process, where electrophile

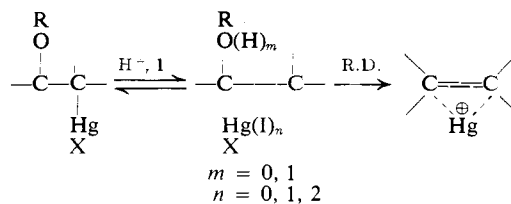
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and/or nucleophile can assist *via* pre-rate-determining coordination. The uncatalyzed cases presumably involve solvent as electrophile and nucleophile.

Direct electrophilic attack at carbon seems to be involved in  $HClO_4$  cleavages of  $R_2Hg$ ,<sup>24</sup> and in the  $Se_2$  processes described by Ingold<sup>25</sup> (solvent nucleophilic participation is not excluded). Nucleophilically catalyzed solvolysis of  $R_FB$  and  $R_FSn$ <sup>26</sup> with solvent alcohol serving as source of the electrophile appear to be a reality. Similar reports exist on the solvolysis of  $CF_3HgI$  by water in the presence of iodide ion, the products in this case being  $CF_3H$  and  $HgI_4^{2-}$ .<sup>27</sup>

In a kinetic study on the brominolysis of phenylboronic acids in aqueous media, Kuivila<sup>28</sup> has also found that fluoride ion accelerates the reaction.

The situation is directly analogous to the current interpretation of  $R-X$  solvolyses.<sup>29</sup> There seems to be increasing evidence that we are *always* dealing with a push-pull mechanism in such cleavage reactions, and that the exact nature of the transition state will be determined by solvent, the leaving group, and the electrophile-nucleophile pair. These views allow an understanding or reinterpretation of many reactions reported in the literature.<sup>30</sup> These will be the subject to a forthcoming review.<sup>31</sup>

**Acknowledgment.** The authors wish to thank the following agencies for their support: Army Research Office (Durham) (USA-DA-ARO-31-124), Petroleum Research Fund (PRF 1086A-4), and National Institute of Health (USPH RG. 9022). Also the authors would like to express their appreciation to Stauffer Chemical Co., Anderson Division, for supplying the triethylboron.

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