pressure and in the cold afforded about 4 g. of oily product which was dissolved immediately with gassing in a small amount of warm benzene and dry ether and cooled to −70°. A crystalline material separated which displayed both B–H and strong O–H stretch in the infrared. The material melted over an indefinite range and smelled strongly of pyridine. Repeated recrystallization afforded 2.5 g. of an unidentified mixture having no B–H stretch but very strong O–H stretch in the infrared. Since the recrystallization procedure employed here was identical with that employed with the other members of the series it must be concluded that pyridine α-naphthylphenylborane is extremely sensitive to traces of moisture.

Reaction of Silver Ion with Pyridine Diphenylborane (I).—To 2.45 g. (0.01 mole) of pyridine diphenylborane dissolved in 10 ml. of acetonitrile was added a solution of 5.0 g. of silver perchlorate in 2 ml. of water and 10 ml. of acetonitrile. After standing at room temperature for two hours the solution was filtered with a tared fritted glass funnel. The silver was washed well with water, ethanol and ether and weighed 0.65 g. which corresponds to 0.6 equivalent of silver per mole of borane. The low yield is no doubt due to the competing hydrolysis and protolysis of borane by water and produced perchloric acid. All other pyridine diarylboranes gave similar qualitative reactions.

Hydrolysis of Pyridine Diphenylborane (I).—To 4.91 g. (0.02 mole) of pyridine diphenylborane dissolved in 60 ml. of acetonitrile was added 5 ml. of water and the solution brought to the reflux temperature in a closed system connected to a wet test meter. Gas was evolved steadily and amounted to 95% of the theoretical amount after correction to S.T.P. The resulting acetonitrile solution was flooded with 300 ml. of water and extracted with two 100-ml. portions of ether. The combined ether extracts were washed with water, dried over magnesium sulfate and the solvent removed in vacuum. The colorless residual oil weighed 4.1 g. and had an infrared spectrum identical with diphenylborinic acid prepared by the acidification of β-aminoethyl diphenylborinate or by the hydrolysis of phenylboron dichloride.

Reaction of Pyridine Diphenylborane (I) with Iodine.—A solution of 245 mg. (1 mmole) of pyridine diphenylborane was prepared in 10 ml. of pyridine. One-ml. aliquots were diluted to 10 ml. with 4:1 pyridine–water and titrated to a yellow iodine end-point with an 0.020 *M* solution of iodine in pyridine. Each aliquot required 4.90 ml. of iodine solution and indicated that the borane was 98% pure if one mole of borane reacts with one mole of iodine.

Reduction of Isobutyryl Chloride with Pyridine Diphenylborane (I).—To 5.3 g. (0.050 mole) of pure isobutyl chloride dissolved in 50 ml. of dry ether was added 12.2 g. (0.050 mole) of pure pyridine diphenylborane (I). The solution was refluxed for five hours with magnetic stirring and cooled to room temperature. An unidentified solid was removed by filtration and the ethereal filtrate combined with 200 ml. of ethanol, 20 ml. of water, 4.0 g. of 2,4-dinitrophenylhydrazine and 2 ml. of concentrated hydrochloric acid. The mixture was heated and stirred for one hour on the steam-bath, flooded with one liter of water and filtered. The precipitated solid was extracted with methylene chloride, the methylene chloride solution concentrated to 20 ml. and placed on a small chromatographic column packed with acid-washed alumina and methylene chloride. The first bright yellow band was collected separately, the solvent evaporated and the residue recrystallized from ethanol–water to yield 6.3 g. or a 50% yield of isobutyraldehyde 2,4-dinitrophenylhydrazone, m.p. 173–176°.[6] Further recrystallization afforded crystals meeting at 181–182°

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[6] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 188, reported m.p. of 182°

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[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, AND THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

Amine Boranes. III. Hydrolysis of Pyridine Diphenylborane and the Mechanism of Hydride Transfer Reactions

BY M. FREDERICK HAWTHORNE AND EDWARD S. LEWIS

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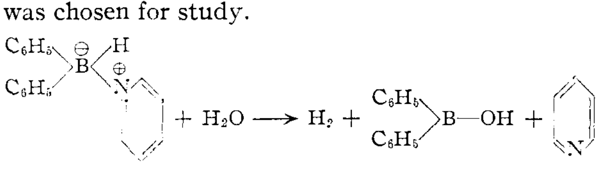
The hydrolysis of pyridine diphenylborane and pyridine diphenylborane-d_1 have both been studied kinetically with water and deuterium oxide in acetonitrile solution. Similarly the hydrolyses of four additional pyridine di-(*p*-x-phenyl)-boranes have been examined and the Hammett treatment applied. It is shown that the results are consistent with a non-linear transition state involving electrophilic attack of a water proton on the electrons of the B–H bond, and it is proposed that electrophilic attacks on bonds to hydrogen are generally of this type.

Pyridine diarylboranes are unique among known arylborane derivatives in that they contain only one B–H bond per molecule and they are therefore well suited for kinetic studies which would examine the chemistry of that bond. Among the simplest of these reactions is the hydrolysis of the B–H bond to produce hydrogen and a B–OH species. Since the hydrolysis of the pyridine diarylboranes was shown[1] to be quantitative and to produce hydrogen and the corresponding boronous acid, this reaction was chosen for study.



Kinetics of the Hydrolysis of Pyridine Diphenylborane.—Since the pyridine diarylboranes were found to be stable in pure acetonitrile, this solvent was employed in the kinetic study. A reaction temperature of 39.90 ± 0.05° was chosen since at this temperature all the compounds examined gave conveniently rapid reactions. The analytical method employed for the determination of the instantaneous concentration of remaining amine borane was based on the previously described[1] titration of hydridic hydrogen with iodine in pyridine solution.

The addition of water to acetonitrile solutions of pyridine diphenylborane produced a rapid second-order reaction, first order both in water and amine borane. The range of water concentration was 0.46 to 4.16 *M* while the pyridine diphenylborane was either 0.05 or 0.10 *M* at low and at high water concentrations, respectively. By using these excess quantities of water the observed reactions were pseudo first-order over-all and were followed to 85%

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[1] M. F. Hawthorne, THIS JOURNAL, **80**, 1293 (1958).

reaction. Curve A of Fig. 1 graphically illustrates the observed kinetic form of the total reaction expressed in (1).

$$\frac{-\mathrm{d}\,[(C_6H_5)_2BH\cdot Py]}{\mathrm{d}t} = k_2[(C_6H_5)_2BH\cdot Py][H_2O] \quad (1)$$

Table I sets forth the data of curve A in which the observed pseudo first-order rate constant, $k = k_2[H_2O]$ is plotted *vs.* water concentration. Table I gives the second-order rate constant for the water reaction.

Initially added pyridine (0.25 *M*) was found to have no effect on the reaction rate. Two runs which employed this addend are found on curve A or in Table I.

TABLE I

KINETICS OF THE HYDROLYSIS OF PYRIDINE DIPHENYLBORANE (PDPB) IN ACETONITRILE SOLUTION AT 39.90 ± 0.05°

Initial concentrations, moles/l.		Pseudo first-order rate constant × 10^6	Second-order rate constant, l./mole sec. × 10^4
PDPB	H_2O		
0.100	2.79	61.5	2.20
.100	1.37	30.5	2.23
.100	0.715	13.9	1.95
.050	4.16	88.2	2.12
.100	2.14	48.0	2.24
.100	1.44[a]	31.8	2.21
.100	3.00[a]	65.2	2.17
.050	0.460	9.1	1.98

[a] Reaction 0.25 *M* with respect to initially added pyridine.

Primary Kinetic Isotope Effects.—Since the hydrolysis of pyridine diphenylborane is first order in both amine borane and water and the reaction rate is not perturbed by added pyridine, it was of interest to determine the primary kinetic isotope effects which might arise from the breaking of the B–H and O–H bonds. This was carried out with deuterium oxide and pyridine diphenylborane-d_1, prepared by the lithium aluminum deuteride reduction of *n*-butyl diphenylborinate in the presence of pyridine.

Curve B of Fig. 1 indicates the kinetics of the reaction of this material with water under the conditions employed with the corresponding protium compound. Table II presents the pseudo first- and the second-order rate constants obtained in these reactions. From these results the primary kinetic isotope effect obtained by the substitution of deuterium for protium on boron has the extremely low value of 1.52.

Substitution of deuterium for protium in the water employed in these reactions led to the data of curve C of Fig. 1. Table II records the pertinent data for these rate measurements and it is seen that this isotope effect is relatively much larger and equal to 6.90.

Curve D of Fig. 1 and Table II record the rate data obtained with pyridine diphenylborane-d_1 *and* deuterium oxide in the same reaction. Comparison of the second-order rate constant for the reaction of pyridine diphenylborane with water and the second-order rate constant obtained with pyridine diphenylborane-d_1 and deuterium oxide produce a double primary kinetic isotope effect of 10.3. Table II presents the rate data obtained for curves B, C and D.

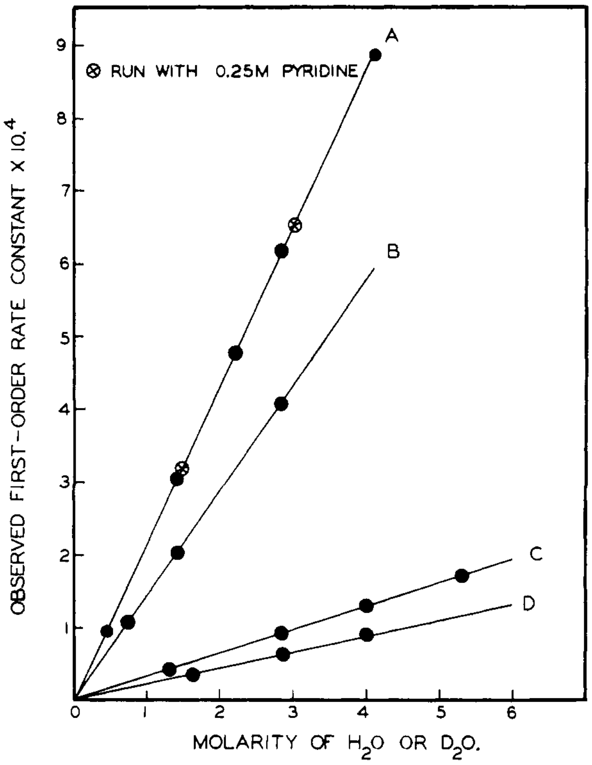

Fig. 1.

Application of Hammett's ρ–σ Treatment to Pyridine Diarylborane Hydrolysis.—Since pyridine di-(*p*-anisyl)-, di-(*p*-chlorophenyl)-, di-(*p*-tolyl)- and di-(*p*-bromophenyl)-boranes were available[1] for study, a Hammett treatment[2] was carried out and a ρ constant evaluated. The substituted amine boranes were each shown to have stabilities in dry acetonitrile which approximated that of pyridine diphenylborane. This was determined by titration of an aliquot of an acetonitrile solution of these compounds after one hour at 39.9°. In every case the titer had not changed by a measurable amount.

TABLE II

RATE DATA FOR DEUTERIUM LABELED RATE RUNS AT 39.90 ± 0.05°

Bond isotope	Initial concentrations, moles/l.		Pseudo first-order rate constant × 10^4	Second-order rate constant l./mole sec. × 10^4
	PDPB	H_2O		
B–D, H–O	0.05[a]	0.75	1.05	1.40
	.10	1.39	2.00	1.44
	.10	2.78	4.03	1.45
B–H, D–O	.10	1.35[b]	0.449	.332
	.10	2.79	0.900	.322
	.10	4.00	1.27	.318
	.10	5.33	1.72	.323
B–D, D–O	.10[a]	1.60[b]	0.35	.219
	.10	2.79	.63	.226
	.10	4.00	.85	.212

[a] Pyridine diphenylborane-d_1. [b] Deuterium oxide.

In order to compare the reactivities of the pyridine diarylboranes under conditions which would give rapid reaction rates, the standard solvent com-

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(2) L. P. Hammett, "Physical Organic Chemistry," 1st edition McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

position was chosen to contain 5.55 M water. Table III contains the pseudo first-order rate constants obtained with each compound at 39.90 ± 0.05° with this standard solvent.

Table III

Pseudo First-order Rate Constants for the Hydrolysis of Di-(p-x-phenyl)-boranes in 5.55 M Water at 39.90 ± 0.05°

Pyridine diarylborane	Initial concentration, mole/l., pyridine diarylborane	Pseudo first-order rate constant $\times 10^3$ sec.$^{-1}$
p-Anisyl	0.20	1.79
	.10	1.74
p-Tolyl	.20	1.44
	.10	1.40
Phenyl	.20	1.14
	.10	1.09
p-Chlorophenyl	.20	0.74
	.10	.78
p-Bromophenyl	.20	.66
	.10	.69

Figure 2 is a Hammett plot of the data of Table III from which a ρ value −0.76 is obtained.

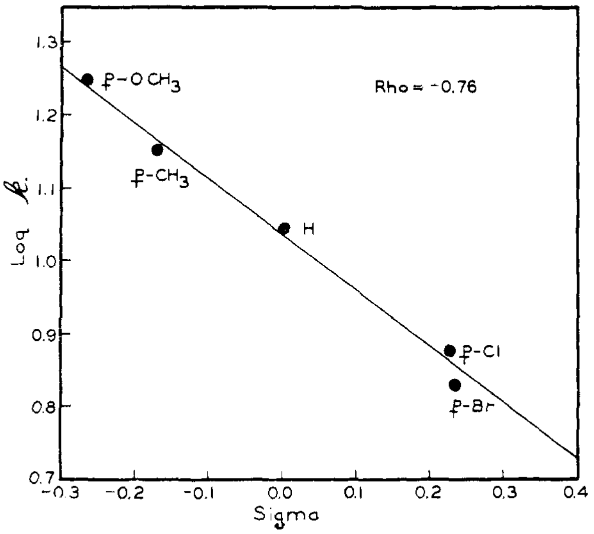
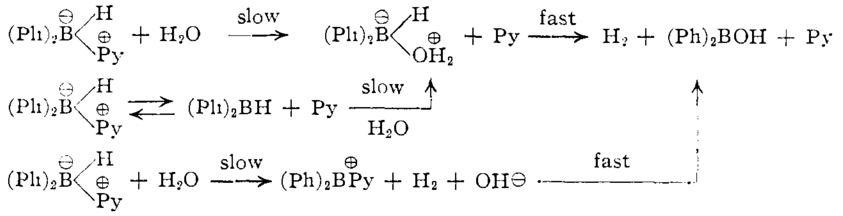


Fig. 2.

Discussion

Mechanism.—The fact that the rate-determining step of the reaction of pyridine diphenylborane with water involves both amine borane and water suggests at least three likely possibilities for describing the over-all process.



$$(\mathrm{Ph})_2\overset{\ominus}{\mathrm{B}}\begin{matrix}\diagup\mathrm{H}\\ \oplus\\ \diagdown\mathrm{Py}\end{matrix} + \mathrm{H_2O} \xrightarrow{\text{slow}} (\mathrm{Ph})_2\overset{\ominus}{\mathrm{B}}\begin{matrix}\diagup\mathrm{H}\\ \oplus\\ \diagdown\mathrm{OH_2}\end{matrix} + \mathrm{Py} \xrightarrow{\text{fast}} \mathrm{H_2} + (\mathrm{Ph})_2\mathrm{BOH} + \mathrm{Py} \quad (2)$$

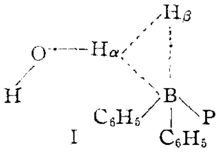
$$(\mathrm{Ph})_2\overset{\ominus}{\mathrm{B}}\begin{matrix}\diagup\mathrm{H}\\ \oplus\\ \diagdown\mathrm{Py}\end{matrix} \rightleftarrows (\mathrm{Ph})_2\mathrm{BH} + \mathrm{Py} \xrightarrow[\mathrm{H_2O}]{\text{slow}} \uparrow \quad (3)$$

$$(\mathrm{Ph})_2\overset{\ominus}{\mathrm{B}}\begin{matrix}\diagup\mathrm{H}\\ \oplus\\ \diagdown\mathrm{Py}\end{matrix} + \mathrm{H_2O} \xrightarrow{\text{slow}} (\mathrm{Ph})_2\mathrm{B}\overset{\oplus}{\mathrm{Py}} + \mathrm{H_2} + \mathrm{OH}^{\ominus} \xrightarrow{\text{fast}} \uparrow \quad (4)$$

Processes 2 and 3 may be eliminated from consideration on the grounds that they leave both the hydrogens almost unaffected in the slow step, which is inconsistent with the substantial isotope effects. This conclusion agrees with the fact that added pyridine did not alter the rate, as it would by process 3, or if the water–diphenylborane were itself formed rapidly and reversibly. Process 4 then remains to represent the observed hydrolysis reaction, since it adequately accounts for the data.

Isotope Effects, ρ Value and Transition State Configuration.—The magnitudes of the observed isotope effects and the low negative value of ρ are of interest from the point of describing the configuration of the transition state. The large effect ($k_{\mathrm{OH}}/k_{\mathrm{OD}}$ = 6.90) when deuterium oxide is substituted for water is nearly as large as that predicted for a complete loss of the OH stretching vibration in the transition state. (Complete loss of a stretching vibration with a fundamental frequency of 3600 cm.$^{-1}$ at this temperature would lead to $k_{\mathrm{OH}}/k_{\mathrm{OD}}$ = *ca.* 9.9, neglecting all other effects.) Large effects of this sort are characteristic of proton transfer process of reasonably high activation energy,[3] although several very rapid reactions of carbanions with methanol gave very small effects. The observed effect of isotopic substitution on boron ($k_{\mathrm{BH}}/k_{\mathrm{BD}}$ = 1.52) is much smaller than that expected for loss of the B–H stretch of 2300 cm.$^{-1}$ ($k_{\mathrm{BH}}/k_{\mathrm{BD}}$ = 4.2) and suggests the conclusion that this vibration is not greatly altered in the transition state. Small isotope effects appear to be the rule for hydride transfer reactions; examples are found in the Cannizzaro reaction,[4] and the hydrolysis of triphenylsilane.[5] The argument that large isotope effects are to be expected in hydride transfer reactions[3] based on the diazonium salt deamination reaction of Melander[6] is only valid if a hydride transfer mechanism is demonstrated. The results of De Tar[7] indicate a facile free radical path for this reaction, and therefore throw substantial doubt on the conclusion. If we accept the generalization that hydride transfer reactions give low isotope effects, a mechanism predicting this result is desirable.

We propose the transition state I for the BH bond hydrolysis and suggest that this sort of non-linear transition state may be general for hydride transfers. It can be seen readily that the attack on the water hydrogen (H_α) is a nucleophilic attack by the



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[3] Several examples are quoted, especially in Tables 5, 7 and 8, in a review of this field: K. S. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[4] K. B. Wiberg, This Journal, **76**, 537 (1954).

[5] S. L. Kaplan and K. E. Wilzbach, *ibid.*, **77**, 1300 (1955).

[6] G. L. Melander, *Arkiv Kemi*, **3**, 525 (1951).

[7] D. F. De Tar and M. N. Turetzky, This Journal, **78**, 3925 (1956).

BH bonding electrons, and occurs from the opposite side of H_α from the oxygen (the electron poor side). The loss of most of the OH_α stretching vibration in this transition state is reasonable, and the large isotope effect follows. The attack on H_β is shown as an attack from the same side of H_β as that to which the boron is attached. The dotted lines suggest the possibility in the use of the pair of electrons in all three atoms. Clearly the motion of the molecule along the reaction coördinate is not closely related to the BH stretching vibration. Thus there is no reason to expect loss of all of the BH stretching vibration in the transition state, and a smaller isotope effect would be predicted. It is probably overly naive to attribute the isotope effect to the loss of zero point energy of the B–H bending vibration, although this would give the correct magnitude, since much of an effect of this size could also come from a mass effect or a small change in the stretching vibration.

The transition state I is therefore quite compatible with the isotope effects but is certainly not uniquely determined. The triangular transition state is also strongly suggested by some analogous reactions. The retention of configuration in electrophilic substitution on carbon[8] requires attack by the electrophile from the same side of carbon as the leaving group. The bridged structure of diborane shows that a (doubly) triangular configuration resulting from the attack of the powerfully electrophilic BH_3 on the BH bonding electrons is actually stable, so that a transition state with this feature is plausible. Finally, the only reasonable point of attack of an electrophile on a bond to hydrogen must be the center of high electron density, that is, the bond, and a linear configuration $H \cdots H \cdots B$ is not to be expected.

The observation of the double isotope effect when both sites contain deuterium is interesting. The effect ($k_H/k_D = 10.3$) is very close to the product of the individual effects at H_α and H_β, and suggests that no entirely unexpected changes occur on isotopic substitution. It is analogous to the observations of Kaplan and Wilzbach that the effect of tritium in the water was about the same for triphenylsilane ($k_H/k_T = 6.96$) as for triphenylsilane-1-*d* ($k_H/k_T = 7.25$) in ethanolic alkali and in piperidine solution where the tritium isotope effects were 3.05 and 3.00 for the protium and deuterium compounds, respectively.[6]

The relatively small negative value of ρ (-0.76) indicates an only slightly electron-deficient boron atom in the transition state. It is difficult to guess whether the transition state I is satisfactory from this point of view. It is certainly less deficient than a linear transition state where the BH electrons are largely removed from the boron. The data do not exclude a concurrent attack of the nucleophilic solvent acetonitrile at the rear of the boron atom, analogous to the simultaneous nucleophilic and electrophilic attacks on triphenylsilane.[6] A variant of such a transition state with nucleophilic attack by OH^- and electrophilic attack by $CH_3C\overset{+}{N}H$ is also possible. It does not appear that this solvent participation is very important, even though it may occur.

The reaction of pyridine phenylborane with 3.0 *M* water under the same conditions was too slow to measure well. The difference is due in part to the lesser electron availability with only two aryl groups around boron instead of three, but it is possible that the diphenyl compound derives additional driving force from relief of crowding about the boron, a manifestation of B strain.[9]

Experimental

Materials.—Acetonitrile was C.P. grade which had been distilled from phosphorus pentoxide and carefully protected from atmospheric moisture. Pyridine was Karl Fischer grade and used without further purification. The preparation of the pyridine diarylboranes was described in the preceding paper of the series. The samples utilized in the kinetic measurements were purified by recrystallization from benzene–ether–pentane and were 96–100% pure on the basis of iodine reduction.

Pyridine diphenylborane-d_1 was prepared by the reduction of *n*-butyl diphenylborinate with lithium aluminum deuteride according to the previously described procedure.[1] The purified material melted sharply at 106–107° and showed a B–D stretching band at 6 μ in the infrared.

Kinetic Procedure.—All rate measurements were carried out at 39.90 ± 0.05°. Solutions of water or deuterium oxide were prepared in pure and dry acetonitrile at 39° and stored in 100-ml. volumetric flasks. In order to carry out a rate determination, the proper amount of solid pyridine diarylborane was weighed into a 10-ml. volumetric flask and placed in the thermostat. The acetonitrile–water solution which had been thermostated previously was added to the line on the reaction flask at zero time and the flask shaken to dissolve the solid. One-ml. aliquots of reaction mixture were withdrawn at intervals, added to 20 ml. of 80% aqueous pyridine and immediately titrated to a permanent iodine color with a 0.01 *M* solution of iodine in dry pyridine. The first-order constant for each rate run was evaluated from a plot of log iodine titer *vs.* time.

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[8] S. Winstein and T. G. Traylor, THIS JOURNAL, **78**, 2597 (1956), and earlier papers; A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

[9] H. C. Brown, *Science*, **103**, 385 (1946), and later papers in THIS JOURNAL.