Table I. ^{13}C NMR Data[a]

	C-1,3	C-3a,7a	C-4,7	C-5,6	PCH_3
2	38.2 (68.4)	128.8 (9.2)[b]	29.4 (14.0)	123.9 (s)	[c]
3	36.8 (67.1)	127.9 (10.4)	29.3 (13.4)	123.8 (1.8)	16.2 (64.1)
4	34.5 (90.9)	127.3 (13.4)	28.7 (16.5)	123.9 (1.8)	
5	35.4 (67.8)	135.6 (9.8)	127.3 (17.1)[d]	127.8 (s)	[e]
6	34.5 (65.9)	135.0 (10.4)	127.4 (11.6)	127.8 (s)	14.5 (64.7)

[a] $CDCl_3$ solutions except 4 (Me_2SO-d_6). Chemical shifts (parts per million) are downfield from internal Me_4Si Values in parentheses are ^{31}P-^{13}C coupling constants, in hertz. [b] Assignment uncertain. [c] Phenyl signals: ipso, 134.3 (92.8); ortho, 129.8 (9.1);[b] meta, 128.9 (12.2);[b] para, 132.1 (3.0). [d] Downfield signal assumed to be merged with C-5,6. [e] Phenyl signals: ipso, 133.0 (92.2);[f] ortho, 129.7 (9.2); meta, 128.6 (11.6); para, 132.0 (3.1). [f] Upfield signal assumed to be merged with signal of ortho.

g (85%) of phospholene oxide **2** as a colorless oil, bp 154–160 °C (0.02 mm), which quickly solidified to a white solid, mp 109–114 °C. Recrystallization from benzene–ligroin gave white plates: mp 120–121 °C; ^1H NMR ($CDCl_3$) δ 2.32–3.16 (m, 8 H, CH_2), 5.71 (s, 2 H, C=CH), 7.20–7.96 (m, 5 H, phenyl H); ^{31}P NMR ($CDCl_3$) δ +49.7; ^{13}C NMR, Table I.

Anal. Calcd for $C_{14}H_{15}OP$: C, 73.03; H, 6.57; P, 13.45. Found: C, 73.22; H, 6.48; P, 13.81.

2-Methyl-1,3,4,7-tetrahydroisophosphindole 2-Oxide (3). Via the general procedure, a reaction mixture containing methylphosphonous dichloride (17.6 g, 0.15 mol), 4,5-dimethylenecyclohexene (12.9 g, 0.12 mol), copper stearate (150 mg), and ligroin (150 mL) was allowed to stand for 25 days. Distillation of the hydrolyzed product (recovered by continuous extraction with $CHCl_3$ for 48 h) gave 18.1 g (92%) of phospholene oxide **3** as a colorless oil, bp 119–124 °C (0.02 mm), which quickly solidified to a white, hygroscopic solid: mp 107–110 °C; ^1H NMR ($CDCl_3$) δ 1.70 (d, $^2J_{PH}$ = 14 Hz, PCH_3), 2.13–2.96 (m, 8 H, CH_2), 5.77 (s, 2 H, C=CH); ^{31}P NMR ($CDCl_3$) +58.1 (D_2O), +68.9; ^{13}C NMR, Table I.

Anal. Calcd for $C_9H_{13}OP$: C, 64.28; H, 7.79; P, 18.42. Found: C, 64.48; H, 7.96; P, 18.45.

2-Hydroxy-1,3,4,7-tetrahydroisophosphindole 2-Oxide (4). Via the general procedure, a reaction mixture containing phosphorus tribromide (40.6 g, 0.15 mol), 4,5-dimethylenecyclohexene (12.9 g, 0.12 mol), copper stearate (150 mg), and ligroin (150 mL) gave after 10 days 15.9 g (78%) of phosphinic acid **4** as a tan solid; mp 181–188 °C. Recrystallization from absolute ethanol gave white needles: mp 189–192 °C; ^1H NMR (Me_2SO-d_6) δ 2.27 (d, $^2J_{PH}$ = 12 Hz, 4 H, PCH_2), 2.64 (s, 4 H, CH_2), 5.72 (s, 2 H, C=CH), 7.76 (br s, 1 H, OH); ^{31}P NMR (Me_2SO-d_6) δ +60.1; ^{13}C NMR, Table I.

Anal. Calcd for $C_8H_{11}O_2P$: C, 56.47; H, 6.52; P, 18.20. Found: C, 56.31; H, 6.26; P, 17.96.

2-Phenylisophosphindoline 2-Oxide (5). To a solution of phospholene oxide **2** (1.7 g, 7.4 mmol) in anhydrous benzene (65 mL) was added DDQ (1.8 g, 8.1 mmol), and the resulting solution was refluxed for 18 h. The reaction mixture was cooled and the precipitated hydroquinone was filtered off and washed with benzene (three 25-mL portions). The filtrate was then washed with 1% NaOH (three 25-mL portions), and the base washes were extracted with benzene (four 25-mL portions). The benzene solutions were combined, dried ($MgSO_4$), and concentrated to give 0.85 g (47%) of the monohydrate of **5** as a white solid: mp 99–102 °C (lit.[9] mp for the monohydrate, 98–100 °C); ^{13}C NMR, Table I.

2-Methylisophosphindoline 2-Oxide (6). To a suspension of phospholene oxide **3** (2.0 g, 11.9 mmol) in 100 mL of anhydrous benzene was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (3.0 g, 13.1 mmol). The resulting mixture was refluxed for 18 h. The precipitated hydroquinone was filtered off and washed with benzene (three 50-mL portions). The filtrates were concentrated to give a dark brown solid residue. A 1% NaOH solution (50 mL) was added to the residue and the resulting solution was extracted continuously for 48 h with chloroform. The chloroform extract was dried ($MgSO_4$), filtered, and concentrated at reduced pressure (finally 0.1 mm) to give a yellow solid. Kugelrohr distillation (120 °C (0.02 mm)) gave 1.3 g (66%) of the phosphindoline oxide **6** as a colorless oil which solidified on standing to a white, hygroscopic solid: mp 84–86 °C; ^1H NMR ($CDCl_3$) δ 1.59 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 2.86–3.53 (m, 4 H, CH_2), 7.22 (s, 4 H, C=CH); ^{31}P NMR (D_2O) δ +73.3; ^{13}C NMR, Table I.

Anal. Calcd for $C_9H_{11}OP$: C, 65.06; H, 6.67; P, 18.64. Found: C, 65.34; H, 6.83; P, 18.47.

2-Hydroxyisophosphindoline 2-Oxide (7). To a suspension of phosphinic acid **4** (2.0 g, 11.8 mmol) in anhydrous benzene (100 mL) was added DDQ (3.0 g, 13.0 mmol), and the resulting mixture was refluxed for 18 h. The precipitated hydroquinone was filtered off and washed with benzene (three 25-mL portions). The filtrate was then concentrated to give a dark brown solid which was washed with ethyl acetate (three 25-mL portions) to give 1.8 g (91%) of isophosphindoline **7** as a tan solid; mp 154–157 °C. Recrystallization from water gave white needles; ^{31}P NMR ($CDCl_3$) δ +71.2. Since the melting point (156–158 °C) did not match the literature value (142–148 °C[4d]), analysis was performed.

Anal. Calcd for $C_8H_9O_2P$: C, 57.15; H, 5.40; P, 18.42. Found: C, 57.41; H, 5.25; P, 18.63.

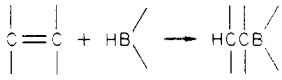
Registry No. 1, 54290-41-4; 2, 70179-63-4; 3, 70179-64-5; 4, 70179-65-6; 5, 50869-62-0; 6, 70179-66-7; 7, 20148-17-8; 8, 2305-26-2; 9, 70179-67-8; 10, 70179-68-9; phenylphosphonous dibromide, 1073-47-8; methylphosphonous dichloride, 676-83-5; phosphorus tribromide, 7789-60-8; *cis*-*N*,*N*,*N*′,*N*′-tetramethyl-4-cyclohexene-1,2-bis(dimethylamine) *N*,*N*′-dioxide, 70179-61-2.

Communications

Unusual Kinetics for the Hydroboration of Alkenes with 9-Borabicyclo[3.3.1]nonane

Summary: Kinetics of the reaction of dimeric 9-borabicyclo[3.3.1]nonane with representative alkenes establishes that hydroboration proceeds through prior dissociation of the dimer into monomer, leading to simplified kinetic expressions, $k_1[(9\text{-BBN})_2]$ for reactive alkenes and $k_{3/2}[(9\text{-BBN})_2]^{1/2}$ [alkene] for less reactive alkenes.

Sir: Hydroboration is a remarkably clean reaction broadly applicable to almost the entire range of unsaturated organic structures[1-3] (eq 1). The addition of the HB< bond

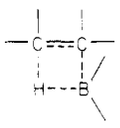


(1)

to the carbon–carbon double bond is cleanly cis.[4] The reaction has been proposed to proceed through a facile 2

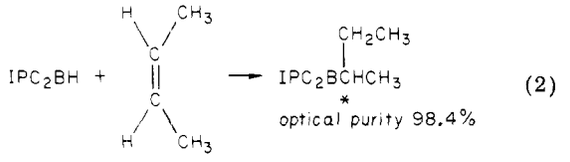
0022-3263/79/1944-2589$01.00/0

+ 2 cycloaddition[5] (1). Moreover, the addition achieves



1

remarkably high stereoselectivities in asymmetric syntheses with optically active reagents such as diisopinocampheylborane (IPC_2BH)[6] (eq 2).



(2)

These fascinating characteristics of the hydroboration reaction have led to considerable speculation, both as to the mechanism of hydroboration[7,8] and the course of the asymmetric synthesis.[9]

It would be desirable to test these speculations against the experimental kinetics. Unfortunately, the determination of such kinetics has been difficult experimentally. Thus the reaction of diborane with olefins generally proceeds through several successive stages involving similar rates.[7d] In order to avoid this difficulty, an early study utilized disiamylborane dimer $(Sia_2BH)_2$.[10] This study indicated the reaction to follow second-order kinetics for a typical olefin, such as cyclopentene (C_5H_8)

$$-\frac{d[(Sia_2BH)_2]}{dt} = k_2[(Sia_2BH)_2][C_5H_8] \qquad (3)$$

In the absence of other data, these results have been considered to be general and have been extrapolated to be representative of all hydroborations.[9b]

Recently, 9-borabicyclo[3.3.1]nonane (9-BBN) has been established as a dialkylborane (dimer) of unusual stability.[11] Accordingly, we undertook to determine the kinetics of hydroboration of representative olefins with this reagent, fully expecting to confirm the kinetics previously observed with $(Sia_2BH)_2$. However, the results surprised us. We observed first-order kinetics with more reactive olefins

$$-\frac{d[(9\text{-BBN})_2]}{dt} = k_1[(9\text{-BBN})_2] \qquad (4)$$

and three-halves-order kinetics with less reactive olefins.

$$-\frac{d[(9\text{-BBN})_2]}{dt} = k_{3/2}[(9\text{-BBN})_2]^{1/2}[\text{olefin}] \qquad (5)$$

In no case did we observe second-order kinetics.

Clearly, these unexpected results require a careful reconsideration of the precise mechanism of hydroboration.

In solvents such as carbon tetrachloride, hexane, cyclohexane, benzene, and tetrahydrofuran (THF), the reagent 9-BBN exists predominantly as the dimer, $(9\text{-BBN})_2$.[12] Solutions of the reagent in these solvents were treated with various olefins and the solutions were maintained at 25 °C. At appropriate intervals of time, aliquots were removed, quenched with excess methanol, and analyzed by GLC for residual olefin. All operations were carried out under nitrogen until the analysis.

In the case of the more reactive olefins, such as 1-hexene, 2-methyl-1-pentene, 3,3-dimethyl-1-butene, and cyclopentene, we observed essentially identical rates. Variation of the olefin concentration did not alter the rate. These results established that the reaction must be first order (eq 4). Typical data for the reaction of cyclopentene are summarized in Table I.[14] Clearly, the calculated first-order rate constants remain virtually identical as the reaction proceeds.

These first-order rate constants are quite similar in solvents other than THF. Thus, cyclopentene reveals a k_1 (10^{-4} s^{-1}) of 1.52 in carbon tetrachloride, 1.97 in hexane, 1.52 in cyclohexane, and 1.95 in benzene. However, in THF k_1 is considerably larger, 10.8.

Less reactive olefins, such as cyclohexene, 1-methylcyclohexene, and 2,3-dimethyl-2-butene, yield rates that are slower and vary with the concentration and the structure of the individual olefin. The kinetics establish these reactions to be first order in olefin and one-half order in 9-BBN dimer (eq 5). Typical kinetic data for cyclohexene are summarized in Table I. Here also the calcu-

Table I. Rate Data and Rate Constants for the Hydroboration of Cyclopentene (0.400 M) and Cyclohexene (0.400 M) with $(9\text{-BBN})_2$ (0.200 M) in Carbon Tetrachloride at 25 °C

time, s	cyclopentene,[a] M	10^4k_1,[b] s^{-1}	time, s	cyclohexene,[a] M	$10^4k_{3/2}$,[b] $L^{1/2}$ $mol^{-1/2}$ s^{-1}
0	0.400		0	0.400	
298	0.382	1.50	6 001	0.339	0.321
1205	0.332	1.54	15 380	0.262	0.343
2713	0.263	1.55	21 605	0.225	0.344
4540	0.202	1.51	42 494	0.148	0.338
6297	0.153	1.52	61 769	0.108	0.336
9001	0.102	1.52	72 007	0.096	0.324

[a] Concentration of $(9\text{-BBN})_2$ is one-half that of olefin. [b] Calculated from the equations $k_1t = 1n\,[b/(b-2x)]$ and $k_{3/2}t = \sqrt{2}\,[(b-2x)^{-1/2} - b^{-1/2}]$, where b is the initial concentration of olefin and $b - 2x$ is the concentration at time t.

(1) Brown, H. C. "Hydroboration"; W. A. Benjamin: New York, N.Y., 1962.
(2) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, N.Y., 1972.
(3) Brown, H. C. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, N.Y., 1975.
(4) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1959**, *81*, 247.
(5) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4708–4712.
(6) (a) Brown, H. C.; Ayyangar, N. R.; Zweifel, G. *J. Am. Chem. Soc.* **1964**, *86*, 397–403. (b) Brown, H. C.; Yoon, N. M. *Isr. J. Chem.* **1977**, *15*, 12–16.
(7) (a) Seyferth, D. in "Progress in Inorganic Chemistry", Vol. III; Cotton, F. A., Ed.; Wiley-Interscience: New York, 1962; p 210. (b) Pasto, D. J.; Kang, S.-Z. *J. Am. Chem. Soc.* **1968**, *90*, 3797–3800. (c) Pasto, D. J.; Lepeska, B.; Cheng, T.-C. *ibid.* **1972**, *94*, 6083–6090. (d) Pasto, D. J.; Lepeska, B.; Balasubramaniyan, V. *ibid.* **1972**, *94*, 6090–6096, (e) Fehlner, T. P. *ibid.* **1971**, *93*, 6366–6373. (f) Jones, P. R. *J. Org. Chem.* **1972**, *37*, 1886–1889.
(8) (a) Dasgupta, S.; Datta, M. K.; Datta, R. *Tetrahedron Lett.* **1978**, 1309–1311. (b) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1075–1082. (c) Clark, T.; Schleyer, P. v. R. *J. Organomet. Chem.* **1978**, *156*, 191–202.
(9) (a) Streitwieser, A., Jr.; Verbit, L.; Bittman, R. *J. Org. Chem.* **1967**, *32*, 1530–1532. (b) Brown, D. R.; Kettle, S. F. A.; McKenna, J.; McKenna, J. M. *Chem. Commun.* **1967**, 667–669. (c) Varma K. R.; Caspi, E. *Tetrahedron*, **1968**, *24*, 6365–6375. (d) Moore, W. R.; Anderson, H. W.; Clark, S. D. *J. Am. Chem. Soc.* **1973**, *95*, 835–844.
(10) Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1961**, *83*, 3417–3422.
(11) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765–7770.
(12) Disiamylborane also exists predominantly as the dimer in both ethyl ether and tetrahydrofuran.[13] See also the data in Table IV of the Ph.D. Thesis (Purdue University) by G. J. Klender.
(13) Brown, H. C.; Klender, G. J. *Inorg. Chem.* **1962**, *1*, 204–214.
(14) The calculations of the rate constants were carried out on a Hewlett-Packard 9820A calculator.

Table II. First-Order and Three-Halves-Order Rate Constants for the Hydroboration of Representative Olefins with (9-BBN)$_2$ in Carbon Tetrachloride at 25 °C

olefin[a]	10^4k_1, s^{-1}	$10^4k_{3/2}$, $L^{1/2}$ $mol^{-1/2}$ s^{-1}
1-hexene	1.54	
2-methyl-1-pentene	1.53	
3,3-dimethyl-1-butene	1.45	
cyclopentene[b]	1.52	
cyclohexene[b]		0.323
1-methylcyclohexene		0.051
2,3-dimethyl-2-butene		0.020

[a] Rate constants in table are for initial concentrations of olefin (0.400 M) and (9-BBN)$_2$ (0.200 M). [b] Variation of the initial concentration of the olefin and (9-BBN)$_2$ did not change the observed rate constants significantly: cyclopentene (0.400 M), (9-BBN)$_2$ (0.100 M), 10^4k_1 1.58; cyclopentene (0.200 M), (9-BBN)$_2$ (0.100 M), 10^4k_1 1.58; cyclohexene (0.400 M), (9-BBN)$_2$ (0.100 M), $10^4k_{3/2}$ 0.324; cyclohexene (0.200 M), (9-BBN)$_2$ (0.100 M), $10^4k_{3/2}$ 0.345.

lated three-halves-order rate constants do not change as the reaction proceeds. The rate constants observed, both for the first-order and three-halves-order kinetics, are summarized in Table II.

Fortunately, the kinetics appear to define the mechanism clearly. Thus the kinetics can be accounted for in terms of a dissociation of the dimer into monomer (eq 6), followed by a reaction of the monomer with the olefin (eq 7).

$$(9\text{-BBN})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ 9\text{-BBN} \qquad (6)$$

$$9\text{-BBN} + \text{olefin} \xrightarrow{k_2} B\text{-alkyl-9-BBN} \qquad (7)$$

This mechanism leads to the following kinetic expression (eq 8), utilizing the usual steady state approximation.

$$-\frac{d[(9\text{-BBN})_2]}{dt} = k_1[(9\text{-BBN})_2]\left(\frac{\frac{1}{2}k_2[\text{olefin}]}{k_{-1}[9\text{-BBN}] + \frac{1}{2}k_2[\text{olefin}]}\right) \qquad (8)$$

If $^1/_2k_2$[olefin] $\gg k_{-1}$[9-BBN], eq 8 reduces to eq 4. Thus the reaction behaves like a unimolecular reaction and exhibits first-order kinetics. However, if $^1/_2k_2$[olefin] $\ll k_{-1}$[9-BBN], eq 8 reduces to eq 5. Thus the reaction exhibits three-halves-order kinetics. For certain olefins, such as 2-methyl-2-butene and *cis*-3-hexene, $^1/_2k_2$[olefin] $\approx k_{-1}$[9-BBN], and the kinetics fail to follow the simplified rate expressions, eq 4 and 5.

This mechanism is supported by a comparison of the relative rates of hydroboration by 9-BBN of certain of these olefins determined competitively with the relative rates calculated from the rate constants. Thus the relative rate, 2-methyl-1-pentene/cyclopentene, gives a competitive value in carbon tetrachloride of 27 (identical with the value in THF[15]), but very different from the ratio of the k_1 values, ~1.00 (Table II). On the other hand, for $k_{3/2}$ reactions, the two values agree closely, 1-methylcyclohexene/cyclohexene 0.159 from the competition experiments and 0.158 from the $k_{3/2}$ values. Since k_1 measures the rate of dissociation of (9-BBN)$_2$, there should be no relationship of the k_1 ratios to the value of k_2, and none is found. On the other hand, k_2 is involved in the measured values of $k_{3/2} = {}^1/_2(k_1/k_{-1})^{1/2}k_2$, so that the ratio of the two $k_{3/2}$ values gives the ratio of the k_2 values and agrees with the values determined competitively.

The question necessarily arises as to why these kinetics are so different from those previously observed with disiamylborane. We are unable to account for these differences. The previous study with disiamylborane involved a much more labile material. Moreover, the dimeric product contains some five different diastereoisomers.[13] Fortunately, these difficulties are avoided with 9-BBN. It is clear that conclusions based on the earlier study with disiamylborane must now be reconsidered.[16]

Herbert C. Brown,* Charles G. Scouten[17] Kung K. Wang

Richard B. Wetherill Laboratory, Purdue University West Lafayette, Indiana 47907

Received February 6, 1979

(15) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297–5301.

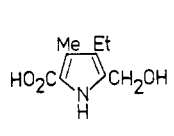
(16) Preliminary qualitative observations on the rate of reaction of pyridine and other tertiary amines with (9-BBN)$_2$ indicated that these reactions also proceed through a prior dissocation of the dimer into monomer. Brown, H. C.; Kulkarni, S. U. *Inorg. Chem.* **1977**, *16*, 3090–3094. A more extensive, more quantitative study is now under way.

(17) (a) Graduate research assistant on Grant GP-6942X of the National Science Foundation, (b) Graduate research assistant on Grant CHE 76-20846 of the National Science Foundation.

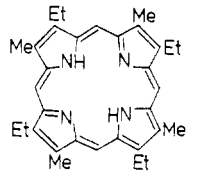
On the Synthesis of Etioporphyrin by Monopyrrole Tetramerization

Summary: Acid-catalyzed tetermerization of 4-ethyl-5-(hydroxymethyl)-3-methylpyrrole-2-carboxylic acid (**1**) is shown to produce a mixture of all four etioporphyrin primary "type-isomers", rather than solely etioporphyrin-I (**2**).

Sir: It was recently reported[1] that acid-catalyzed tetramerization of 4-ethyl-5-(hydroxymethyl)-3-methylpyrrole-2-carboxylic acid (**1**) (bearing a ^{15}N label at position 1) affords an isomerically pure sample of etioporphyrin-I (**2**). This claim, based only on NMR analysis at 100 MHz,



1



2

suggested an extremely facile route to the pure "type-isomer" **2** which would have advantage over presently used procedures.[2] However, we were surprised at the apparent homogeneity of the sample since: (1) such monopyrrole polymerizations normally[3] give a mixture of all four primary type-isomers; (2) a similar monopyrrole tetramerization in the coproporphyrin series was originally claimed[4] to give pure type-III isomer, but this was subsequently corrected[5] in favor of random type-isomer formation; and

(1) Momenteau, M.; Mispelter, J.; Loock, B.; Lhoste, J. M. *Can. J. Chem.* **1978**, *56*, 2598–2603.
(2) Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1471–1475.
(3) Smith, K. M. in "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier, Amsterdam, 1975; p 32.
(4) Bullock, E.; Johnson, A. W.; Markham, E.; Shaw, K. B. *J. Chem. Soc.* **1958**, 1430–1440.
(5) Kay, I. T. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, *48*, 901–905.

0022-3263/79/1944-2591$01.00/0