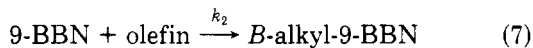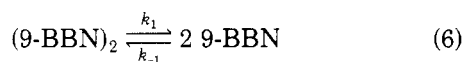Table II. First-Order and Three-Halves-Order Rate
Constants for the Hydroboration of Representative
Olefins with (9-BBN)$_2$ in Carbon Tetrachloride at 25 °C

olefin[a]	$10^4 k_1$, s^{-1}	$10^4 k_{3/2}$, 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), $10^4 k_1$ 1.58; cyclopentene (0.200 M), (9-BBN)$_2$ (0.100 M), $10^4 k_1$ 1.58; cyclohexene (0.400 M), (9-BBN)$_2$ (0.100 M), $10^4 k_{3/2}$ 0.324; cyclohexene (0.200 M), (9-BBN)$_2$ (0.100 M), $10^4 k_{3/2}$ 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 $^1/_2 k_2$[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 $^1/_2 k_2$[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, $^1/_2 k_2$[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]

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(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,
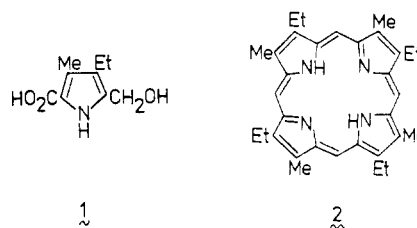
suggested an extremely facile route to the pure "type-isomer" 2 which would have advantage over presently used procedures.[2] However, we were surprised at the apparent homogeneity of the sample since: (1) such monopyrrole polymerizations normally[3] give a mixture of all four primary type-isomers; (2) 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.
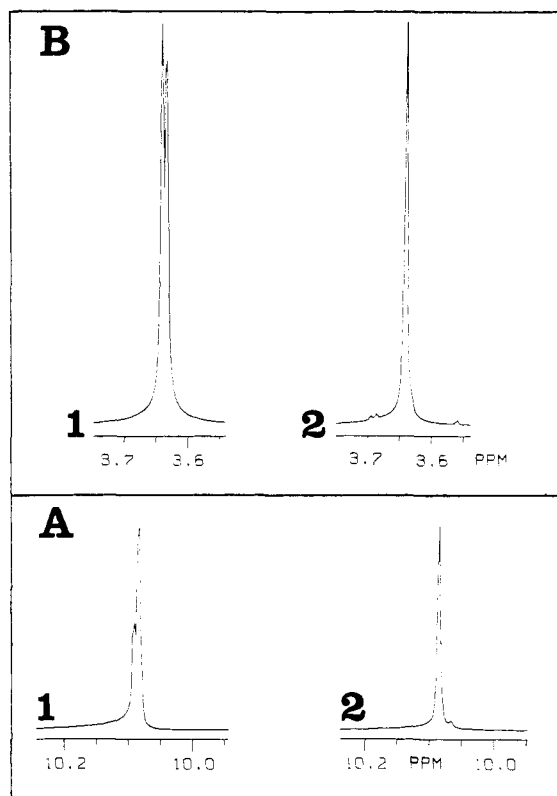(2) Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* 1972, 1471–1475.
(3) Smith, K. M. in "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier, Amsterdam, 1975; p 32.
(4) Bullock, E.; Johnson, A. W.; Markham, E.; Shaw, K. B. *J. Chem. Soc.* 1958, 1430–1440.
(5) Kay, I. T. *Proc. Natl. Acad. Sci. U.S.A.* 1962, 48, 901–905.

(15) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* 1976, 98, 5297–5301.
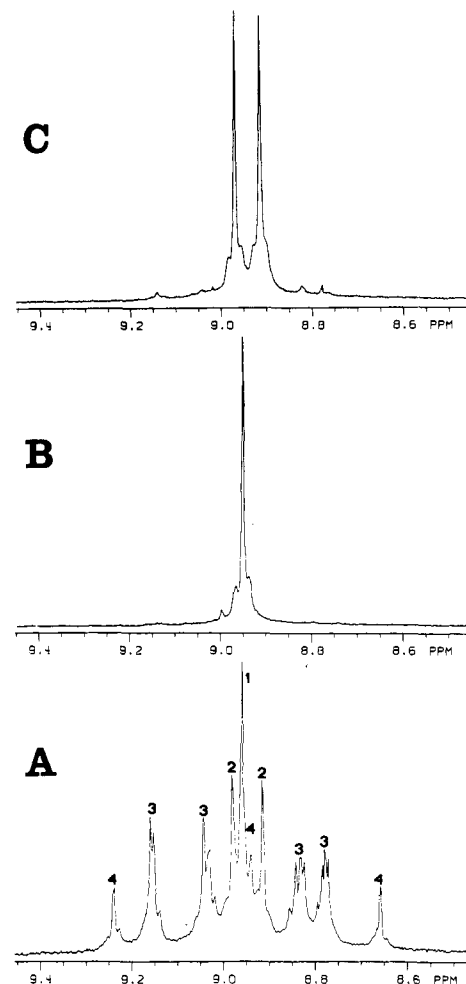
Figure 1. 360-MHz NMR spectra (Nicolet NT-360) in $CDCl_3$ of: (A1) meso protons of etioporphyrin from acid-catalyzed tetramerization of 1; (A2) meso protons of pure etioporphyrin-I;[2] (B1) nuclear methyls of etioporphyrin from acid-catalyzed tetramerization of 1; (B2) nuclear methyls of pure etioporphyrin-I (2).

(3) the 60- or 100-MHz NMR spectra of the individual etioporphyrin type-isomers are somewhat similar.[6]

We have repeated exactly the synthesis[7] of porphyrin from 1 as described [yield, 37% (lit.[1] yield, 35.3%)] in the ^{14}N series. The 100-MHz NMR spectrum of the product gave an initial impression of pure type-isomer formation (i.e., singlet meso protons, quartet and triplet for the ethyl groups), except that the nuclear methyl groups were an unresolved doublet (assigned in the ^{15}N series to a heteronuclear coupling with the central nitrogens by the original authors,[1] though no similar coupling with the equidistant ethyl methylenes was observed).

At 360 MHz the situation is very clear. Figure 1 shows the meso-proton resonances (A) of the etioporphyrin from 1 and of pure etioporphyrin-I,[2] as well as the nuclear methyls (B) from 1 and pure material. Clearly, the etioporphyrin from 1 is an isomeric mixture.

The nature of the mixture was established by preparation of the mercury(II) "double-sandwich" complexes.[6] In Figure 2A the 360-MHz NMR spectra of the meso protons in the mercury complex from the monopyrrole tetramerization are shown. Above the spectrum are shown the corresponding spectra for the pure etioporphyrin-I mercury complex (B) and for the pure etioporphyrin-II mercury complex (C).[6] The tetramerization material,

Figure 2. 360-MHz NMR spectra (Nicolet NT-360) in $CDCl_3$ of the meso protons in mercury(II) "double-sandwich" complexes from: (A) etioporphyrin from acid-catalyzed tetramerization of 1; (B) pure etioporphyrin-I;[2,6] (C) pure etioporphyrin-II.[6] The arabic numerals (1–4) above peaks in A refer to the resonances from mercury(II) complexes of etioporphyrins-I through -IV, respectively. The etioporphyrin-II complex in C is contaminated with a little of type-III.[6] Shoulders on peaks are due to [199]Hg–[1]H couplings.

Figure 2A, is an obvious mixture,[8] and the same spectra at 100 MHz were equally convincing.

We therefore reiterate that acid-catalyzed monopyrrole tetramerizations yield all four primary type-isomers. Regularly substituted isomers (e.g., type-I) must be prepared, at the present state of synthetic expertise, from dipyrroles.[2]

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(6) Hudson, M. F.; Smith, K. M. *Tetrahedron* **1975**, *31*, 3077–3083.

(7) A solution of 3.4 g of pyrrole 1 and 680 mg of potassium ferricyanide in 14 mL of acetic acid was heated under reflux for 1 h with vigorous stirring. The mixture was then allowed to stand at room temperature for 3 days before collection of the precipitate, washing with methanol, and drying. This crude material was chromatographed on Woelm neutral alumina (Brockmann Grade 1), eluting with chloroform; the product (823 mg) was crystallized from $CHCl_3$–methanol.

(8) A *very rough* integration of the spectrum in Figure 2A indicates the composition of the mixture to be approximately: 15% type-I (2); 25% type-II; 50% type-III; 10% type-IV.