# Mass Spectrometric Characterization of Petroporphyrins[1]

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**Abstract:** Mass spectra of the porphyrins obtained by acid extraction from a number of asphaltenes showed that the petroporphyrins are not homogeneous. Up to a dozen homologs of both the deoxophyllo and etio series are present in a Gaussian-like distribution with a band width of three to five methylene groups. High-resolution mass spectrometry on selected major peaks showed only the presence of alkyl porphyrins with no oxygen functional groups. Chromatographic separation of the petroporphyrins confirmed the presence of etio and phyllo series porphyrins and indicated the presence of a small amount of material of the rhodo series. The possible significance of these findings on the geochemistry of formation of the petroporphyrins is discussed.

The structure of petroporphyrins[2] has been a subject of investigation since Treibs' discovery of this class of compounds 30 years ago. In a series of papers Treibs described the separation of porphyrins from a variety of natural bituminous materials including oil, shale, and coal.[3] He identified the materials as etioporphyrin III (Etio) and deoxophylloerythroetioporphyrin (DPEP). On the basis of this identification, Treibs then put forward a degradative scheme by which chlorophyll a or b could be converted to DPEP and hemin to Etio. Treibs described his scheme in terms of six types of reactions: (1) demetalation, (2) saponification, (3) reduction, (4) aromatization, (5) decarboxylation, and (6) chelation. Application of these six steps to chlorophyll a (Figure 1a) would yield vanadyl DPEP (Figure 1b). The same types of reactions would convert chlorophyll b and bacteriochlorophyll to the same end product. The important point to note is that this scheme yields only one product, DPEP. If the starting material were hemin, Etio would be the final product.

Following Treibs' discoveries, many workers have devised methods of separation and identification of the porphyrins from bituminous materials. These studies in the main have broadened and tended to confirm Treibs' ideas as to the source and method of formation of the petroporphyrins, and his thesis has stood the test of time without any major revisions or extensions. There have, however, been scattered indications that the porphyrins in petroleum were not a single species but rather a series of compounds, some with molecular weights considerably higher than vanadyl Etio or vanadyl DPEP.[4–8] However, no definite proof has been offered, and, therefore, a mass spectrographic investigation was undertaken.

## Results

The porphyrins used in this study were obtained by extraction from asphaltenes with methanesulfonic acid (MSA).[9] Mass spectra were obtained on an AEI MS-9 double-focusing mass spectrometer. The conditions in the spectrometer source were selected so that no thermal rearrangements occurred, and essentially only molecular ions were recorded. Reference to Table I shows that the knowledge of the mass of an unknown porphyrin makes it possible to assign it to certain classes. For example, porphyrins of the etio and phyllo series must have molecular weights of 310 + 14$n$, where $n$ is an integer. Likewise, porphyrins with an isocyclic ring (deoxophylloerythro series) must have molecular weights of 308 + 14$m$, where $m$ is an integer 2 or greater.

**Table I.** Molecular Weights of Alkyl-Substituted Porphyrins

| $n^a$ | Etio or phyllo series | Deoxophylloerythro series[b] |
|---|---|---|
| 8 | 422 | 420 |
| 9 | 436 | 434 |
| 10 | 450 | 448 |
| 11 | 464 | 462 |
| 12 | 478 | 476[c] |
| 13 | 492 | 490 |
| 14 | 506 | 504 |
| 15 | 520 | 518 |
| 16 | 534 | 532 |
| 17 | 548 | 546 |
| 18 | 562 | 560 |

[a] Number of methylene groups attached to the porphyrin nucleus. [b] The presence of an isocyclic ring leads to molecular formulas with two less protons than the etio type. [c] Deoxophylloerythroetioporphyrin.

In Figure 2 the mass spectrum of a sample of Boscan petroporphyrin is given. The major peaks in the

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(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) The use of the term "petroporphyrins" to describe the plurality of porphyrins found in petroleum was originated by Professor A. H. Corwin: see, for example, Paper V-10, A. H. Corwin, 5th World Petroleum Congress, New York, N. Y., 1959; also, A. H. Corwin, W. S. Caughey, A. M. Leone, J. E. Danieley, and J. F. Bagli, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1957, Preprints, 2, No. 4, p A-35; A. H. Corwin, a report to the Petroleum Research Fund Advisory Board of the American Chemical Society, March 1957. Professor Corwin suggested that a special name for these materials was justified because of indications that at least some of the components were not identical with known porphyrins. The work reported here confirms that these materials do constitute a new class of naturally occurring compounds. The designation of this class of porphyrins as "petroporphyrins" seems appropriate and conforms to the accepted practice of allowing the person who first recognizes the unique nature of a material the right to name it.

(3) A. Treibs, *Angew. Chem.*, 49, 682 (1936), and references therein.

(4) L. K. Beach and J. E. Shewmaker, *Ind. Eng. Chem.*, 49, 1157 (1957).

(5) M. F. Millson, D. S. Montgomery, and S. R. Brown, *Geochim. Cosmochim. Acta*, 30 (2) 207 (1966).

(6) G. Costantinides and G. Arich, Paper V-11, 6th World Petroleum Congress, Frankfurt, Germany, 1963.

(7) R. A. Dean and E. V. Whitehead, Paper V-9, 6th World Petroleum Congress, Frankfurt, Germany, 1963.

(8) A. H. Corwin and E. W. Baker, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., March 1964, Preprints 9, No. 1, p 19, and references therein.

(9) J. G. Erdman, U. S. Patent 3,190,829 (June 22, 1965).

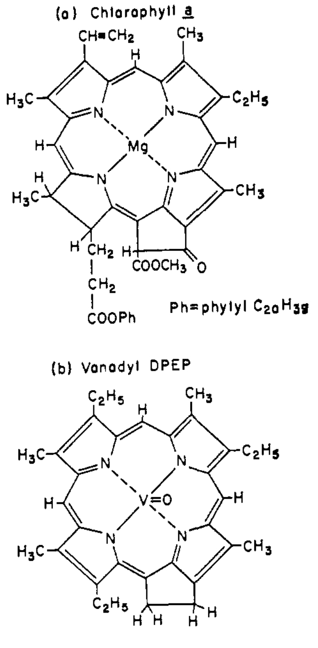

Figure 1. Structure of chlorophyll a and vanadyl DPEP.

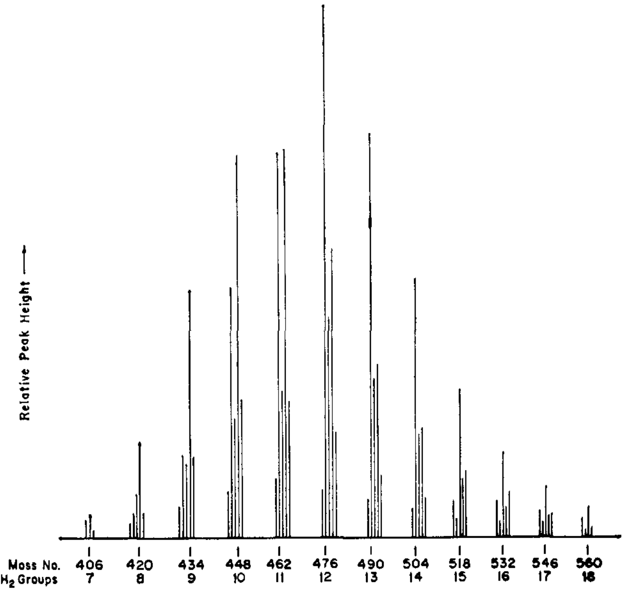

Figure 2. Mass spectrum of Boscan petroporphyrin.

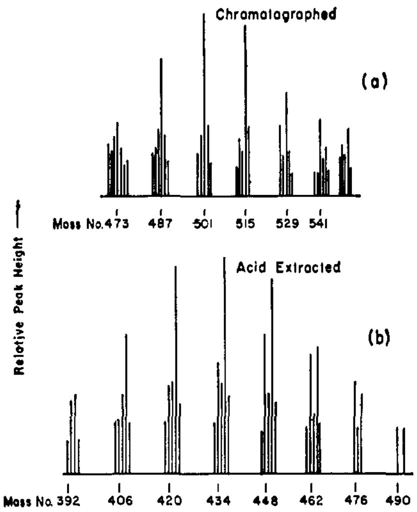

Figure 3. Low-voltage mass spectrum of porphyrins from Wilmington crude.

spectrum are those of porphyrins of the deoxophylloerythro series. Approximately a dozen different porphyrins of this series are present encompassing those with as few as eight methylene groups to as great as 18 or even 19. DPEP itself (12 $CH_2$ groups) is the largest component comprising *ca.* 25% of the mixture. The quantities of the other porphyrins of this series fall off in a symmetrical way with increasing or decreasing molecular weights. Accurate mass measurements of a number of selected peaks (Table II) showed that these parent peaks represent alkyl porphyrins, and specifically that they contain no oxygen. The closest molecular formula of an oxygen containing porphyrin is some 30 millimass (mM) units from the observed mass, whereas the accuracy of the mass measurement appears to be about 2.5 mM units. Thus, we conclude that the higher molecular weight components of the mixture are not the result of incomplete loss of oxygen, but are actually alkyl porphyrins, some of which must possess side chains longer than two carbons, since 18 or 19 methylene groups must be distributed over the eight $\beta$ positions on the porphyrin.

**Table II.** Accurate Mass Determination of Selected Peaks in Boscan Petroporphyrins

| Nominal peak mass | | | Δ, mM[b] |
|---|---|---|---|
| 434 | Obsd mass[a] | 434.2446 | |
| | Calcd for $C_{29}H_{30}N_4$ | 434.2473 | 2.7 |
| | Calcd for $C_{28}H_{26}N_4O$ | 434.2108 | 33.8 |
| 476 | Obsd mass | 476.2928 | |
| | Calcd for $C_{32}H_{36}N_4$ | 476.2906 | 2.2 |
| | Calcd for $C_{31}H_{32}N_4O$ | 476.2576 | 35.2 |
| 504 | Obsd mass | 504.3233 | |
| | Calcd for $C_{34}H_{40}N_4$ | 504.3253 | 2.0 |
| | Calcd for $C_{33}H_{36}N_4O$ | 504.2889 | 34.4 |
| 506 | Obsd mass | 506.3392 | |
| | Calcd for $C_{34}H_{42}N_4$ | 506.3409 | 1.7 |
| | Calcd for $C_{33}H_{38}N_4O$ | 506.3045 | 34.7 |

[a] Resolution *ca.* 1 in 20,000, mass measured by peak matching against perfluoro-*t*-butylamine. [b] Difference between observed mass and calculated mass in millimass units.

The question of whether acid extraction of the porphyrins leads to the production of artifacts or loss of peripheral groups has been raised.[10] Therefore, experiments were undertaken to obtain samples of native porphyrin which could be compared spectrometrically with that obtained by acid extraction.

A sample of petroporphyrin from Wilmington crude was obtained by chromatographic methods. To avoid the possibility that degradation might occur during the separation, the chromatographic substrates were selected so that no highly active (acidic) sites would be present. Thus, only deactivated alumina and silica gel were used with relatively nonpolar solvents. Five chromatographic separations with intermediate partitioning between dimethylformamide and hexane produced a material of a purity of about 20%. It is possible to obtain a mass spectrum on such an impure

(10) M. Blumer, *Anal. Chem.*, 33, 1288 (1961).

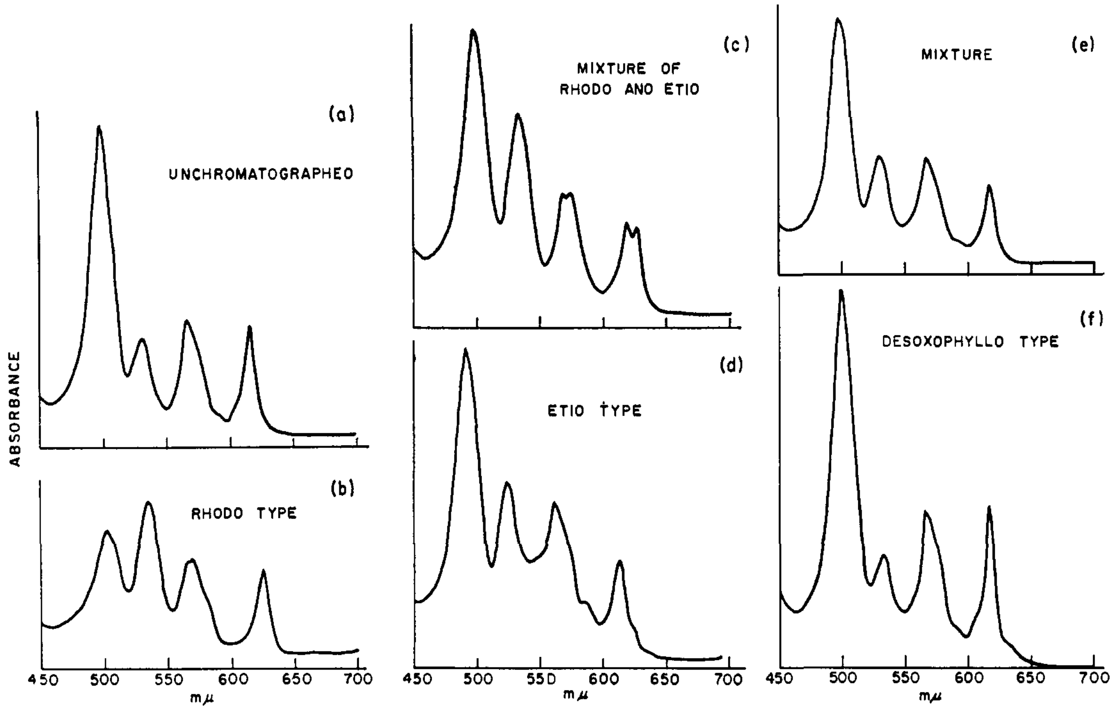

Figure 4. Visible spectra of petroporphyrins from Boscan asphaltene (see text for details).

material since the porphyrin peaks are readily recognizable above the background. A portion of the mass spectrum is shown in Figure 3a. During the separation every effort was made to prevent fractionation of the vanadyl porphyrins so that the sample would be representative of the natural porphyrin mixture.

A second sample of Wilmington petroporphyrin was prepared by the MSA extraction method. The significant portion of its mass spectrum is shown in Figure 3b. These spectra are compared in Table III. In the first column are shown the masses of the major peaks. In the next column, 65 mass units (the mass of VO minus two protons) are subtracted to give the mass of the porphyrin from which the chelate was derived. In the final column are the masses of the major peaks of the free base porphyrin recovered by MSA extraction. It will be noted that the correspondence between these peaks is one to one.

Table III. Comparison of Molecular Weights of Petroporphyrins Separated by Acid Extraction and by Chromatography

| Method of separation<br>Form of porphyrin | Chromatographic<br>Vanadyl chelate | | Acid extraction<br>Free base |
|---|---|---|---|
| | *m/e* | −65[a] | *m/e* |
| | 543 | 478 | 478 |
| | 541 | 476 | 476 |
| | 529 | 464 | 464 |
| | 515 | 450 | 450 |
| | 501 | 436 | 436 |
| | 487 | 422 | 422 |
| | 473 | 408 | 408 |

[a] Subtraction of 65 mass units from the mass of the vanadyl chelate gives the mass of the free base porphyrin from which this chelate was formed.

The conclusion may be drawn that at least in Wilmington crude and probably in all others no significant alteration of the porphyrins occurs during the acid extraction and subsequent work-up.

**Chromatographic Separation of Boscan Petroporphyrins.** A partial chromatographic separation of the Boscan petroporphyrins into spectral types has been accomplished. The visible spectra of the cuts from silica gel chromatography are shown in Figure 4. In Figure 4a, the spectrum of the unchromatographed petroporphyrin is shown. This spectrum is similar to that reported by a number of workers as being typical of the petroporphyrin.[11] The spectrum in Figure 4b is that of a rhodoporphyrin. This represents a relatively small amount of material and might be dismissed as an artifact of the separation scheme, but other evidence suggests that it is real. This fraction with a rhodo-type spectrum was present in all of the petroleum asphaltene samples examined. A fraction with a similar type spectrum taken from the Athabasca tar has been the subject of an extensive investigation by Millson, Montgomery, and Brown.[5] Cut 2 (Figure 4c) is clearly a mixture and is the result of incomplete resolution of the rhodo type (cut 1) and etio type (cut 3). Cut 4 (Figure 4e) is probably also an unresolved mixture. Cut 5 (Figure 3) is a typical deoxophylloerythroetio type. This is one of the largest fractions obtained and has been crystallized.

In Figure 5 is shown a mass spectrum of cut 3 which was referred to as an etio type by reference to its visible spectrum. The wide spread in molecular weight from 394 to 562 representing *ca.* 6 to 18 methylene groups will be noted. The mass spectrum confirms that the material which has major peaks at 464, 478, 492, etc., is mainly of the etio series, while the peaks at 2 mass units less, *i.e.*, 462, 476, 490, show the presence of a considerable amount of the deoxophylloerythro series remaining. The fact that the maximum is at mass 450

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(11) H. N. Dunning, J. W. Moore, and A. T. Myers, *Ind. Eng. Chem.*, **46**, 2000 (1954).

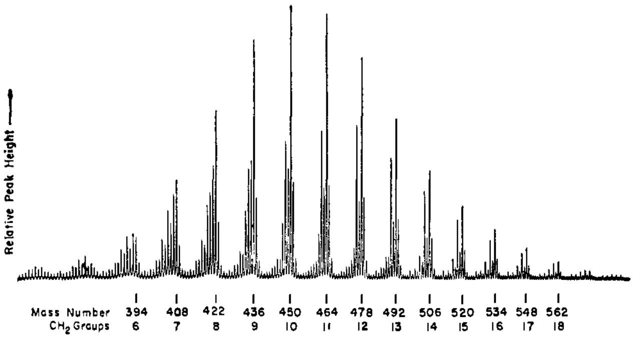

Figure 5. Low-voltage mass spectrum of Boscan petroporphrin enriched Etio fraction (see text for details).

rather than at 478 also is noteworthy. Such a drift toward lower average molecular weight is typical of the results as the samples were further purified by chromatography. Apparently some fractionation did occur with the higher molecular weight materials being concentrated in the tails of the peaks and, thus, were lost as the chromatography was terminated before the last trace was recovered from the columns.

This figure illustrates the degree of separation that has been achieved on single columns, the width of the envelope of molecular weights present, and some of the pitfalls in the purification.

It was felt that a comparison of the porphyrins from different sources would be interesting. The materials selected and their origins are given in Table IV. Samples of porphyrins suitable for spectrometric examination were obtained from a number of different asphaltenes by the MSA extraction and chromatographic purification method.

Table IV. Mass Distribution of Some Petroporphyrins

| Source | *m/e* of most abundant porphyrin | Approximate half-width of envelope[a] Mass units | $CH_2$ units |
|---|---|---|---|
| Boscan asphaltene[b] | 476 | 70 | 5 |
| Mara asphaltene[b] | 450 | 70 | 5 |
| Mara gas oil[c] | 436 | 56 | 4 |
| Gilsonite[d] | 476 | No envelope | |
| Wilmington asphaltene[e] | 436 | 42 | 3 |
| Boscan asphaltene (phyllo fraction) | 462 | 42 | 3 |
| Boscan Asphaltene (etio fraction) | 450 | 70 | 5 |

[a] Taken as the number of mass units up and down from the most abundant peak to the grouping approximately $^1/_{10}$th the concentration of the most abundant peak. [b] Boscan and Mara crudes are of Venezuelan origin; the asphaltene fraction was obtained by precipitation with pentane. [c] Vacuum distillate of equivalent atmospheric boiling point 700–1050°F. [d] Asphaltene fraction; obtained from Cowboy Vein, Uinta Basin, Utah. [e] California origin.

A condensation of these data is presented in Table IV. Interestingly, the porphyrin obtained from gilsonite did not exhibit the Gaussian-like mass distribution characteristic of the petroleum porphyrins. In fact, one predominant peak at 476, the mass of deoxophylloerythroetioporphyrin, with small amounts of materials at lower masses was observed. It has been reported that only nickel chelates are present in gilsonite.[12]

All of the other samples are similar in that both etio-type and deoxophyllo-type materials are present. There are, however, some interesting differences in the average mass of the porphyrins from different sources. For example, the *average* porphyrin from Boscan contains 12 methylene groups while that from Wilmington contains only 9. Also, the range of the masses of porphyrins is somewhat different, the range in Boscan being the largest. This difference is indicated in Table IV as the approximate number of methylene groups seen on the mass spectrum above and below the most abundant peak.

## Discussion

These studies show that the porphyrin fractions of crude petroleum are extremely complex mixtures. Not only do the relative amounts of rhodo, etio, and phyllo porphyrins vary with source, but the molecular weights vary both in average and distribution. In addition, each molecular peak is probably due to many isomers rather than a single compound.

As pointed out earlier, the degradation scheme proposed by Treibs leads only to one final product from chlorophyll, that is DPEP. This scheme does not accommodate the presence of a number of homologs which we and others have shown to be present. A number of other investigators have also noted the multiplicity of porphyrins present. Morandi and Jensen[13] state that the porphyrins in oil shale are compounds of at least three homologous series. Dean and Whitehead[7] have noted that vanadyl porphyrins from a crude petroleum showed parent mass peaks in the range of $C_{28}$–$C_{33}$. Thomas and Blumer[14] showed that porphyrin extracted from an oil shale of Swiss origin contained pigments with a range of $C_{27}$–$C_{34}$. These authors also noted that such a discovery compelled an explanation beyond that offered in Treibs' scheme. They suggested that the compounds of masses 490–492 and 504–506 (those containing one or two more carbon atoms than DPEP and Etio) might be accounted for by a reduction of the carboxyl groups to an alkyl group with the same number of carbons. However, the presence of porphyrins with masses of 518 to 560 cannot be accounted for by such a mechanism.

We suggest that the observed Gaussian-like distribution of molecular weights requires an additional process beyond those listed by Treibs. After consideration of the possibilities, we feel that the most likely explanation is a transalkylation reaction.

The nearest analogy, although admittedly somewhat tenuous, is the Jacobsen rearrangement.[15] The Jacobsen rearrangement, generally considered as the acid-catalyzed migration of methyl groups from one position to another in aromatic systems, has an additional very interesting feature; *i.e.*, some products are the result of a cross migration of alkyl groups. Thus, tetramethyl-

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(12) J. M. Sugihara and L. R. McGee, *J. Org. Chem.*, **22**, 795 (1957).
(13) J. R. Morandi, and H. B. Jensen, *J. Chem. Eng. Data*, **11**, 81 (1966).
(14) D. W. Thomas and M. Blumer, *Geochim. Cosmochim. Acta*, **28**, 1147 (1964).
(15) P. deMayo "Molecular Rearrangements," Part I, Interscience Publishers, Inc., New York, N. Y., 1963, p 301.

benzene reacts to produce some trimethyl- and pentamethylbenzenesulfonates. These rearrangements proceed rapidly under conditions where the aromatic system is protonated. In the case of the aromatic systems strong acids are required; the porphyrins, on the other hand, are much stronger bases, requiring only organic acids for protonation. It would appear that sufficiently high temperatures and geologic time could produce the observed migrations. A further example of the relative ease of the loss of peripheral groups from the porphyrins is the production of deuteroporphyrin from protoporphyrin by the loss of two vinyl groups. This reaction is carried out in about 0.5 hr in fused resorcinol at 160–180°. The mechanism has not been established but is generally referred to as a transvinylation reaction, either ionic or free radical. While no direct evidence in favor of any mechanism can be offered, transalkylation *via* an ionic or free-radical mechanism could help to account for the multitude of reaction products observed.

## Experimental Section

Asphaltenes were prepared in the standard way by precipitation from the crude petroleum with 10 parts of pentane at room temperature. The precipitated asphaltenes were rewashed with pentane and recovered by filtration or centrifugation. Some samples were further purified by exhaustive Soxhlet extraction. The petroporphyrins were prepared by extraction from the asphaltenes with methanesulfonic acid.[9] The porphyrins were recovered from the methanesulfonic acid by extraction with methylene chloride and purified by chromatography over silica gel with cyclohexane–benzene–ether. Visible absorption spectra were taken on a Beckman DK-1 recording spectrophotometer. Mass spectra were taken on an AEI MS-9 double-focusing mass spectrometer, fitted with a direct sample insertion lock. Source temperatures and ionizing potential were selected to give only parent molecular ions. Typical conditions were 230–250° and 7–9 ev.

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# *Communications to the Editor*

## A Novel Biscyclopropylcarbinyl System[1]

*Sir:*

We wish to report the preparation and some of the chemical behavior of two novel epimeric biscyclopropylcarbinols which are of interest as nonclassical carbonium ion precursors,[2a] as well as in other connections.[2b]

The compounds in question were derived from the recently reported[2c] II-COOH, mp 185° dec, which was in turn obtained from the Simmons–Smith reaction on the methyl ester of dihydrohydrindacenecarboxylic acid[2c] (I). Acid II-COOH reacts readily with Pb$(OAc)_4$ and pyridine in benzene solution[3] even at room temperature to give a *ca.* 60% yield of an acetate[4] II-OAc, mp 92–93°, whose nmr spectrum $(CCl)_4$ shows a singlet at $\tau$ 4.32 for the $C_4$ $\alpha$-proton, an AB quartet with $J_{AB} = 6$ cps, $\tau_A$ 9.50 and $\tau_B$ 9.62 for four cyclopropane protons, and an AB quartet with $J_{AB} = 14$ cps, $\tau_A$ 7.62 and $\tau_B$ 8.22 for the two $C_8$ protons. Solvolytically, this acetate is one of the most reactive *secondary* esters ever encountered.[2a] Thus, attempted saponification with methanolic KOH gives only partially the saponification product, II–OH, along with considerable solvolysis product, II-OMe. The latter,[4] bp 82–84° (4 mm), is obtained exclusively when the acetate is refluxed in methanol for 10 min. The nmr spectrum ($CCl_4$) of II-OMe, showing a singlet for the $\alpha$-proton at $\tau$ 6.24, is consistent with the indicated structure.

The high solvolytic reactivity of II-OAc provides an effective route to the parent hydrocarbon and thus direct evidence regarding the relative configurations of the two cyclopropane groups. In 65% aqueous diglyme containing concentrated $NaBH_4$, acetate II-OAc is converted rapidly at 50° to the parent hydrocarbon[4] II-H, bp 92° (4 mm). No alcohol product is observed, so carbonium ion trapping[5] by the $BH_4^-$ is extremely efficient, indicating a relatively stable and long-lived cationic intermediate. Acetate II-OAc is also converted to hydrocarbon II-H, but less smoothly, by hydrogenolysis with $PtO_2$ catalyst in ethanol. The nmr spectrum ($CCl_4$) of hydrocarbon II-H shows an AB quartet for the four $C_4$ and $C_8$ protons with $J_{AB} = 15$ cps, $\tau_A$ 8.01 and $\tau_B$ 8.17, and another AB quartet for the four cyclopropane protons with $J_{AB} = 5$ cps, $\tau_A$ 9.77 and $\tau_B$ 10.05. This spectrum, indicating two kinds of proton on $C_4$ and $C_8$, contrasts with that of hydrocarbon VI which has a *trans* relationship of the two cyclopropane methylenes. The two hydrocarbons are also distinguishable and separable by vpc.

The *trans* hydrocarbon VI may be obtained from the dihydrohydrindacene[4] III, mp 90°, which is obtained in 80% yield from Birch reduction of *s*-hydrindacene.[6] In its nmr spectrum ($CCl_4$), III shows a singlet signal

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(1) Reported in part at the Annual Meeting of the Japanese Chemical Society, Osaka, Japan, April 4, 1965, and the Japanese–American Seminar in Physical Organic Chemistry, Kyoto, Japan, April 6–10, 1965.

(2) (a) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966); (b) L. Birladeanu and T. Hanafusa, unpublished work; (c) T. Hanafusa, L. Birladeanu, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3510 (1965).

(3) (a) E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963); (b) J. K. Kochi, *ibid.*, **87**, 1811, 2500 (1965).

(4) The indicated compounds gave satisfactory carbon and hydrogen analyses.

(5) (a) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962); *J. Am. Chem. Soc.*, **85**, 2324 (1963); (b) S. Winstein, A. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(6) R. T. Arnold and E. Rondestvedt, *ibid.*, **67**, 1265 (1945).