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Volatile Silicon Complexes of Etioporphyrin I[1]

The presence of several homologous series of porphyrins have been demonstrated in some oil shale rocks, shale oils, and petroleums.[2,3] However, the application of microanalytical techniques (i.e., mass spectrometry and gas chromatography) to structure determination has been limited due to the low volatility of the porphyrin components.

We would like to report the synthesis of several novel Si(IV) etioporphyrin I derivatives and the effects that their various additional silicon ligands have on porphyrin volatility as measured by gas chromatography at normal pressure.

The treatment of etioporphyrin I with silicon tetrachloride or hexachlorodisiloxane[4] and anhydrous pyridine in a sealed glass tube at 185°C for 6 hours, followed by hydrolysis of the residue in dilute aqueous, ethanolic hydrochloric acid, gave after purification on alumina, a 60% yield of product A. The absorption spectrum was metalloporphyrin-like with Soret band at $\lambda_{max}^{CHCl_3}$ 535 mμ (ε = 314,000), and two longer wavelength bands at $\lambda_{max}^{CHCl_3}$ 535 mμ (ε = 11,700), and $\lambda_{max}^{CHCl_3}$ 572 mμ (ε = 13,800). The mass spectrum of A showed a strong molecular ion at m/e 538, followed by a more intense peak at m/e 521 corresponding to the loss of an -OH ligand. Thus the structure dihydroxy-Si(IV)-etioporphyrin I was indicated.

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(1) Work supported, in part by National Aeronautics and Space Administration and U. S. Atomic Energy Commission.

(2) E. W. Baker, T. F. Yen, J. P. Dichie, R. E. Rhodes, and L. F. Clark, J. Am. Chem. Soc., 89, 3631 (1967).

(3) R. L. Levy, H. Gesser, E. A. Halevi, S. Saidman, J. Gas Chromatog., 2, 254 (1964).

(4) R. D. Joyner and M. E. Kenney, Inorg. Chem., 1, 236 (1962).

Silylation of A with bis(trimethylsilyl)acetamide in pyridine gave a product B, subliming at 145°C (.05 mm Hg). Mass spectral analysis of the sublimate showed predominant ions at m/e 682 and m/e 593. The fragment m/e 593 was the most intense peak corresponding to loss of one ligand of 89 mass units [$OSi(CH_3)_3$]. Thus B was assigned the structure bis(trimethylsiloxy)-Si(IV)-etioporphyrin I.

Compounds C, D, F, G, H, I, K (Table I) were isolated from a complex mixture of products produced when the contents of the sealed tube reaction were treated with ethanol or t-butanol. Trimethylsilylation of D and I gave compounds E and J respectively. Mass spectral analysis indicated that the predominant high mass fragmentation was due to loss of one ligand. In silicon complexes where two different ligands were present, such as in compounds D, E and G, predominant high mass fragmentation ions occurred at both mass (M-x) and (M-y).

Preliminary gas chromatographic analysis of the silicon complex porphyrins was accomplished on an 11' x 1/4" ID glass column packed with 1% (OV-1) [methylsilicone phase] coated 100-120 mesh smooth glass beads. The temp. was kept isothermal at 250°C and a helium carrier flow of 27 ml/min was used. Each chromatographic peak was collected and identified by mass spectrometry. Etioporphyrin I, Ni(II)-etioporphyrin I, and diethoxy-Si(IV)-etioporphyrin I (C) would not chromatograph under the described conditions. However, bis(trimethylsiloxy)-Si(IV)-etioporphyrin I (B) showed a marked increase in volatility and could be chromatographed despite an increase in molecular weight of 88 mass units over the diethoxy-silicon complex. The increased volatility can be attributed, at least in

part, to the shielding of the aromatic porphyrin ring by the bulky trimethylsiloxy groups above and below the porphyrin plane. Consideration of the GC retention times (Table I) indicates that additional ligand bulkyness (E to H, J, K) does not render the porphyrin nucleus more volatile than B but seems to vary directly with the molecular weight.

In the past, standard gas chromatography has had no practical use in porphyrin separations.[5] The results of our preliminary study indicate that conversion of porphyrins into volatile tetravalent silicon derivatives should provide a means by which microquantities of complex mixtures of homologous series, such as those found in ancient biogenetic deposits, can be separated and structurally studied using a gas chromatography-mass spectrometry combination. This work will also be expanded to include development of a rapid quantitative means for positive identification of porphyrins and chlorins extracted from recent biological sources.

Acknowledgment. We are grateful to Dr. G. Eglinton for useful discussions.

(5) E. Klesper, A. H. Corwin, and D. A. Turner, J. Org. Chem., 27, 700 (1962).

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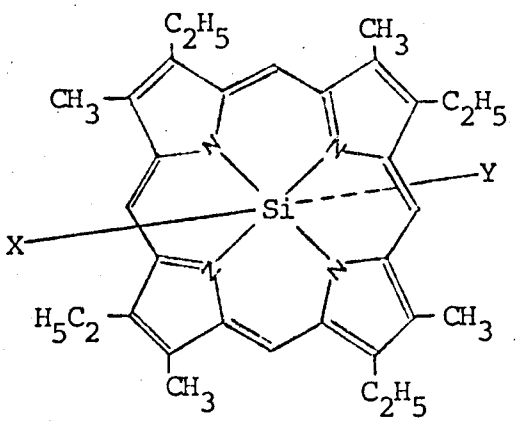
Table I. Gas Chromatographic Retention Times[a] and Predominant 70eV Mass Spectral Ions[b] of X,Y-Si(IV) etioporphyrins



Compd	X (Ligand)	(Y) Ligand	m/e M^+	m/e $[M-(X \text{ or } Y)]^+$
A	OH	Y=X	538	521
B	$OSi(CH_3)_3$	Y=X	682	593
C	OCH_2CH_3	Y=X	594	549
D	$OSi(OCH_2CH_3)_3$	OH	700	683,521
E	$OSi(OCH_2CH_3)_3$	$OSi(CH_3)_3$	772	683,593
F	$OSi(OCH_2CH_3)_3$	Y=X	862	683
G	$OSiOC(CH_3)_3(OCH_2CH_3)_2$	$Y = X_H$[c]	946	739, 711
H	$OSi(OC[CH_3]_3)_2OCH_2CH_3$	Y=X	974	739
I	$OSi(OC[CH_3]_3)_2OH$	Y=X	918	711
J	$OSi(OC[CH_3]_3)_2OSi(CH_3)_3$	Y=X	1062	783
K	$OSi(OC[CH_3]_3)_3$	Y=X	1030	767

[a]The following gas chromatographic retention times were observed: Compound B (11 min), E (14 min), F (17 min), G (21 min), H (25 min), J (>27 min), K (>27 min).

[b]All mass spectra were obtained using an AEI MS-12 mass spectrometer equipped with a solid sample probe.

[c] X_H = Ligand X on compound H.

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