

CHROM. 7034

Note

High-pressure liquid chromatography of metallocarboranes*

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(Received September 6th, 1973)

With the development of highly efficient, commercially available high-pressure liquid chromatographs, applications of this powerful separation method in organic chemistry and biochemistry have been reported in increasing numbers. Few reports of the application of this chromatographic technique in the area of transition metal organometallic chemistry have been made, however. This, of course, reflects the current needs of this relatively new area of chemistry, as is exemplified by the sub-field of metallocarboranes. The initial studies of metallocarboranes, discovered in 1965¹, required only column chromatography to purify the main products investigated². A comprehensive study of the nine isomers of $C_5H_5CoC_2B_9H_{11}$ necessitated more powerful techniques and preparative thick-layer chromatography was employed³. Now that chemical investigations in the metallocarborane area are more detailed, and a wider variety of closely related species can be synthesized, the application of high-pressure liquid chromatography (HPLC) has become a necessity. We describe here several applications of this technique to metallocarboranes to demonstrate the usefulness of HPLC in organometallic chemistry.

INSTRUMENTATION AND EQUIPMENT

The chromatograph was constructed primarily with parts obtained from Waters Ass. The pumping system was comprised of a 1000 p.s.i. Milton Roy reciprocating positive displacement minipump modified by Waters Ass. with three damping devices. The pump was connected to a septum injector unit containing two Viton-A septa by stainless-steel tubing (0.02 in. I.D.) and Swagelok fittings. The injector was attached to either three stainless-steel columns (4 ft., 0.303 in. I.D.) connected in series for preparative-scale separations, or to a stainless-steel column (3 ft., 0.09 in. I.D.) for analytical use. The columns were packed by standard methods⁴ with Waters Porasil-A, a silica gel packing with a 37-75- μ particle diameter. The last column was connected by 1-mm I.D. plastic tubing to an LKB 8300A Uvicord II photometer which operated at 280 nm and contained a detector cell of 100- μ l volume. The photometer was connected to an LKB 7000 UltroRac fraction collector.

Samples consisted of solutions of the metallocarboranes saturated in the

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eluting solvent and were injected with either a Pressure-Lok syringe (Precision Sampling Corp.) or a Hamilton gas tight syringe.

RESULTS AND DISCUSSION

One common method of metallocarborane synthesis, involving addition of a transition metal chloride and sodium cyclopentadienide to a solution of a reduced carborane dianion, characteristically produces a wide variety of products⁵. This polyhedral expansion reaction applied to 1,6- $C_2B_8H_{10}$ using $CoCl_2$ produces two closely related metallocarboranes $C_5H_5CoC_2B_8H_9(C_2B_8H_9)$ and $C_5H_5CoC_2B_8H_{10}$ (ref. 5). The spectral and chromatographic similarity of a metallocarborane and its substituted derivative is a common problem in this area³. These two products were isolated by column chromatography as a single purple fraction apparently pure by thin-layer chromatography (TLC). The 1H -nuclear magnetic resonance spectrum suggested that a mixture was present and preparative-scale HPLC in hexane- CH_2Cl_2 (7:2) effected the separation, allowing full characterization of the two products. A 30-mg sample was eluted with a flow-rate of 2.4 ml/min resolving $C_5H_5CoC_2B_8H_9(C_2B_8H_9)$ at a retention volume of 610 ml, and $C_5H_5CoC_2B_8H_{10}$ at 700 ml.

A different type of separation problem resulted when the polyhedral expansion reaction was applied to 1,10- $C_2B_8H_{10}$ (ref. 5). A yellow fraction initially separated from the reaction mixture by column chromatography was found to contain a mixture of $C_5H_5CoC_2B_7H_9$ and $C_5H_5CoC_2B_9H_{11}$ by mass spectroscopy. The particular isomers of these two types of metallocarboranes formed in this reaction had identical R_F values determined by TLC. The metallocarboranes 2,3,10- $C_5H_5CoC_2B_7H_9$ and 1,2,9- $C_5H_5CoC_2B_9H_{11}$ as well as several other minor components from the yellow fraction were separated by preparative-scale HPLC in hexane. A 20-mg sample was used with a flow-rate of 2.6 ml/min. The retention volumes of the main components 2,3,10- $C_5H_5CoC_2B_7H_9$ and 1,2,9- $C_5H_5CoC_2B_9H_{11}$ were 584 and 857 ml, respectively.

Recently we have used⁶ HPLC to monitor kinetic data on thermal polyhedral rearrangements. The red 4,1,6- $C_5H_5CoC_2B_{10}H_{12}$, (I), rearranges to the orange 4,1,8-isomer, (II), at 45°. A further isomerization to the red-orange 4,1,12- $C_5H_5CoC_2B_{10}H_{12}$, (III), occurs at 66° (ref. 7). The spectral properties of the three isomers are so similar that usual methods for obtaining kinetic data cannot be employed. (I) is readily separated from (II) and (III) in 7 min with the analytical column using hexane- CH_2Cl_2 (3:2). Separation of (II) and (III) requires 18 min using hexane- CH_2Cl_2 (9:1). Correction for the difference in absorptivity at 280 nm is straightforward and excellent kinetic data have been obtained in this manner.

We have also made use of this high-pressure system in other common chromatographic applications such as routine checks of sample purity. In studies involving compounds such as the metallocarboranes which have low volatility and are susceptible to thermal reactions, precluding the use of gas chromatography, we have found that the application of HPLC, as discussed here, can be of great importance.

ACKNOWLEDGEMENT

We gratefully acknowledge the support of the work by N.A.S.A. (subgrant NCL 05-007-003).

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