SYNTHESIS AND NMR SPECTRA OF 2,2,2-TRIDEUTERIOETHYLARSINE AND 2,2,2-TRIDEUTERIOETHYLCYCLOPENTAARSINE

A.L. RHEINGOLD * and S. NATARAJAN

Department of Chemistry, State University of New York College at Plattsburgh, Plattsburgh, New York 12901 (U.S.A.)

(Received September 8th, 1981)

Summary

Pentakis(2,2,2-trideuterioethyl)cyclopentaarsine (PDECA) was synthesized by the reaction of 2,2,2-trideuterioethylarsine with dibenzylmercury. Variable temperature NMR spectra in C_6D_6 are interpreted in terms of fast pseudorotation. NMR and mass spectra and synthesis of 2,2,2-trideuterioethylarsine are also described.
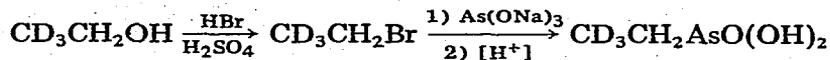
Introduction

The interpretation of the solution dynamics of pentaorganocyclopentaarsines, *cyclo*-$(AsR)_5$, from NMR spectroscopic and viscosity data has led to several conflicting conclusions. Thorough and critical discussions of previous results and their varying interpretations have been published [1,2]. One of the more serious remaining inconsistencies in interpretation is the extraordinary differences reported for the rates of ring pseudorotation for $(AsMe)_5$ (PMCA) and $(AsEt)_5$ (PECA). Whereas PMCA's rate of pseudorotation is NMR-rapid at —100°C, West et al., have analyzed the NMR spectra of PECA recorded at 120°C in terms of five overlapping ethyl group resonances implying that pseudorotation is NMR-slow [3,4]. Although it has been previously suggested that the seemingly unreasonable 220°C difference could be resolved by reinterpreting the spectra of PECA as three complex A_2B_3 (or ABC_3) patterns (instead of five first-order ethyl patterns) [2], verification through simulation has not been possible because of the large number of spin groups (up to 15) involved.

We report now the synthesis and NMR data for $(CD_3CH_2As)_5$ (PDECA) which would be expected to display either three or five AB patterns (or single lines if $\Delta\nu$(AB) is unresolvable). The properties of $CD_3CH_2AsH_2$, the precursor to the cyclopentamer, are also presented.

---

* Author to whom correspondence should be addressed at the Department of Chemistry, University of Delaware, Newark, DE 19711 (U.S.A.)

Results and discussion

Pentakis(2,2,2-trideuterioethyl)cyclopentaarsine $(CD_3CH_2As)_5$ was prepared according to the following scheme:

$$CD_3COOD \xrightarrow{PCl_3} CD_3COCl \xrightarrow{LiAlH_4} CD_3CH_2OH$$

$$CD_3CH_2OH \xrightarrow[H_2SO_4]{HBr} CD_3CH_2Br \xrightarrow[2)\ [H^+]]{1)\ As(ONa)_3} CD_3CH_2AsO(OH)_2$$

$$CD_3CH_2AsO(OH)_2 \xrightarrow{Zn,\ H_2SO_4} CD_3CH_2AsH_2 \xrightarrow{(PhCH_2)_2Hg} (CD_3CH_2As)_5$$

Conventional methods [5] for preparing cyclopolyarsines by reducing the appropriate arsonic acid with aqueous hypophosphorous acid are very sensitive to the presence of traces of sodium halide, obtained along with the arsonic acid, and of acids and other trace-level, water-soluble impurities. Dibenzylmercury
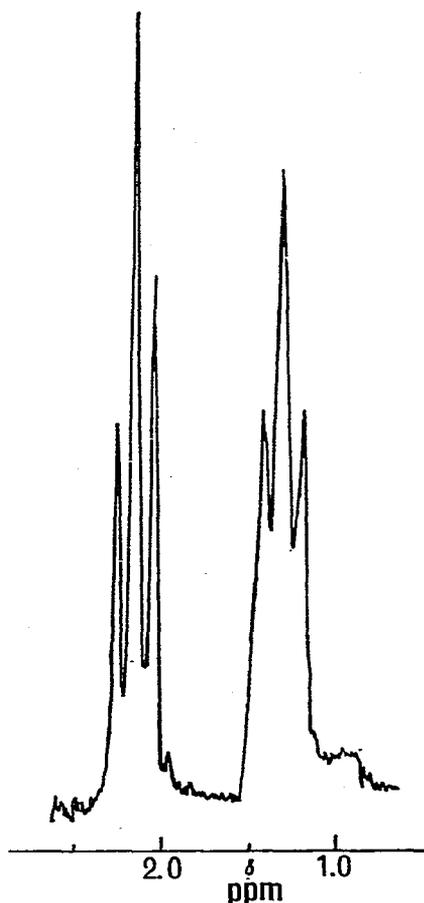

Fig. 1. Proton magnetic resonance spectrum of 2,2,2-trideuterioethylarsine at 32°C. Line broadening from residual ^{75}As coupling is used to assign the upfield resonance to the As bound protons.

in benzene is a convenient and general reagent for the formation of homoatomic catenates from alkylphosphines and arsines [6]. This system avoids the trace impurities in aqueous media which cause polymerization of cyclopolyarsines. Dibenzylmercury readily converts alkyl-phosphines and -arsines to the cyclo-pentamers (RP)$_x$ or (RAs)$_x$ ($x = 5$ and R = alkyl group) under mild conditions. Mercury and toluene formed in the reaction along with the cyclic pentamer can be easily removed. $CD_3CH_2AsH_2$ was prepared by reducing the arsonic acid by the Zn and H_2SO_4 method [2].

$CD_3CH_2AsH_2$

The 60 MHz NMR spectrum of $CD_3CH_2AsH_2$ in benzene is shown in Fig. 1. The upfield triplet, δ 1.27 ppm, shows the effect of quadrupolar broadening (width, half-height 6.1 Hz) from As^{75} ($I = 3/2$) and must, therefore, be assigned to the AsH$_2$ group. The CH$_2$ protons produce also a triplet, δ 2.15 ppm (width, half-height 1.2 Hz); J(HH) = 7.1 Hz. The chemical shifts for the CH$_2$ and AsH$_2$ groups in $CD_3CH_2AsH_2$ are unusual in that they would appear to be assigned incorrectly based upon the chemical shifts previously observed for CH$_3$AsH$_2$ (also in benzene); CH$_3$ (δ 1.11 ppm) and AsH$_2$ (δ 2.30 ppm) [7], but the observed effects of quadrupolar broadening must be considered definitive. The apparent upfield shift for the AsH$_2$ group may result from neighbor aniso-tropic shielding effects [8].

The mass spectral data for $CD_3CH_2AsH_2$ including major peaks and probable assignments are given in Table 1. The base peak appears at m/e 109 (M^+). In comparison with the mass spectrum of CH$_3$AsH$_2$ [9], the peak at m/e 107 is most likely $CD_3CH_2As^+$. The almost complete absence of peaks due to As—D species indicate that H—D exchange is of limited significance.

The gas-phase infrared spectrum of $CD_3CH_2AsH_2$ (see Table 2) shows strong

TABLE 1

MASS SPECTRUM OF CD$_3$CH$_2$AsH$_2$

m/e	Relative abundance (%)	Assignment
109	100	CD$_3$CH$_2$AsH$_2^+$
108	7	CD$_3$CH$_2$AsH$^+$
107	20	CD$_3$CH$_2$As$^+$, CD$_2$CH$_2$AsH$_2$, CD$_3$CHAsH$^+$
106	8	CD$_3$CHAs$^+$, CD$_2$CHAsH$_2^+$
105	9	CD$_3$CAs$^+$, CD$_2$CAsH$_2^+$, CD$_2$CH$_2$As$^+$
104	11	CD$_2$CHAs$^+$, CDCH$_2$AsH$^+$, CDCHAsH$_2^+$
103	9	CD$_2$CAs$^+$, CDCH$_2$As$^+$, CDCHAsH$^+$
102	45	CDCHAs$^+$
101	3	CDCAs$^+$
92	5	CH$_3$AsH$^+$
91	10	CH$_3$AsH$^+$
90	10	CH$_3$As$^+$
89	9	CH$_2$As$^+$
79	8	AsH$_2$D$^+$
78	30	AsH$_3^+$
77	7	AsH$_2^+$
76	51	AsH$^+$
75	7	As$^+$

TABLE 2

INFRARED SPECTRUM OF $CD_3CH_2AsH_2$

Frequency a (cm^{-1})	Assignment
2750—2900s	C—H stretch
~2080s	C—D + As—H stretch
1740m	overtone
1440m	CH$_2$ deformation
~1205s	CH$_2$ wag
1060m	CD$_3$ deformation
940vs(br)	As—H$_2$ deformation
860s	As—H$_2$ wag
710m	CH$_2$ rock

a s = strong; vs = very strong; m = medium; b = broad.

absorption due to As—H stretch and C—D stretch, but are unresolvable due to overlap in the region of 2080 cm^{-1}.

(CD$_3$CH$_2$As)$_5$

In the absence of symmetry, each proton in each methylene group in $(CD_3CH_2As)_5$ is chemically unique and would generate five AB NMR patterns if $\Delta\nu(AB)$ is large enough to resolve, or five distinct lines if too small to resolve. These predictions are anticipated if the solution structure is similar to the puckered asymmetric solid-state configuration found by X-ray scattering and electron diffraction in PMCA [10,11]. $(CD_3CH_2As)_5$, however, displays neither of the anticipated patterns but instead a 2 : 3 or 2 : 2 : 1 NMR pattern (depending on dilution) [12] in C_6D_6 indicating the presence of a permanent or time-averaged plane of symmetry, as is also found for PMCA. The phenomena responsible for symmetry generation are discussed in detail for $(ClCH_2As)_5$ in the literature [2]. Initially $(CD_3CH_2As)_5$ shows peaks in the integrated ratio of 2 : 3 (δ 2.07, 2.19 ppm). No weak upfield peaks attributable to polymeric or oxidized species as have been observed in PMCA [6] are seen initially in PDECA, but do appear after several days' storage.

It must therefore be concluded that the rate of pseudorotation in PDECA is NMR-rapid in the temperature range studied (—65 to 75°), in agreement with the observations for PMCA, and that the inherently anisochronous methylene protons are unresolvable.

Experimental

NMR spectra were recorded on a R20B Hitachi-Perkin Elmer spectrometer with an attached variable temperature unit. Mass spectra were recorded on a Du Pont 21-492B spectrometer (70 eV ionizing potential, 4×10^{-6} mmHg pressure). Infrared spectra were recorded in the gas phase using 10 cm pathlength gas cells and a Perkin Elmer IR spectrometer 223. Volatile, air-sensitive materials were handled in an all-glass vacuum system.

Acetic acid-d_4 supplied by Aldrich Chemical Company was used as the precursor for preparing the cyclic pentamer $(CD_3CH_2As)_5$.

CD$_3$COCl, CD$_3$CH$_2$OH, and CD$_3$CH$_2$Br were prepared by the standard methods [13].

(i) CD$_3$COCl: Acetic acid-d_4 (40 g) was treated with 20 ml of PCl$_3$ in a 100 ml 3-necked flask equipped with a condenser for downward distillation. On heating the mixture in a water bath, CD$_3$COCl distilled off (b.p. 45—50°C). A second distillation gave a pure sample boiling at 50°C (33 g—64% yield).

(ii) CD$_3$CH$_2$OH: CD$_3$COCl (32 g) was reduced with LiAlH$_4$ (22 g) in dry n-butyl ether. Fractionation after removing the excess LiAlH$_4$ gave 15 g of CD$_3$CH$_2$OH (b.p. 78—80°C) (85% yield).

(iii) CD$_3$CH$_2$Br: The bromide was prepared by treating CD$_3$CH$_2$OH (13.2 g) with 55 ml 48% HBr and 8.8 ml conc. H$_2$SO$_4$. CD$_3$CH$_2$Br boiling at 38—45°C was collected (13.2 g, 43%) and used without further purification in the next step.

(iv) CD$_3$CH$_2$AsO(OH)$_2$: The arsonic acid was prepared by the Quick and Adams method [5] using CD$_3$CH$_2$Br (0.108 mol) (iii), 10.8 g As$_2$O$_3$ (0.0544 mol) and 10 M (33 ml) NaOH solution. The mixture was refluxed and vigorously stirred for 72 h and the arsonic acid was isolated by standard methods. After several recrystallizations from an ethanol-water mixture, required to remove all traces of NaBr, the acid's m.p. was 102°C.

(v) CD$_3$CH$_2$AsH$_2$ was synthesized by reducing CD$_3$CH$_2$AsO(OH)$_2$ with Zn and H$_2$SO$_4$ [2].

Arsonic acid (iv) (7 g) in 70 ml 3 M H$_2$SO$_4$ was added over a period of 1 h to 35 g Cu-coated Zn (prepared by treatment with 5 g CuSO$_5$ · 5 H$_2$O) in 75 ml H$_2$O in a 3-necked (1-liter) evacuated flask attached to a vacuum line. The flask was cooled in an ice-water bath. The volatile contents were collected in a series of traps (—45°C, —78°C and —196°C). The —78°C trap contained mostly CD$_3$CH$_2$AsH$_2$ and traces of moisture. The —45°C trap contained H$_2$O, and the —196°C trap contained only AsH$_3$. CD$_3$CH$_2$AsH$_2$ was purified by passing it several times through —45°C and —78°C traps and a molecular sieve column until the molecular weight by the vapor density method gave a value of 108.2 (calcd, 109.0) (0.73 g, 15%).

Pentakis(2,2,2-trideuterioethyl)cyclopentaarsine (CD$_3$CH$_2$As)$_5$—PDECA

CD$_3$CH$_2$AsH$_2$ (0.534 mmol) was distilled from a storage bulb on a vacuum line into a repeatedly degassed hexadeuteriobenzene solution of dibenzyl-mercury (0.534 mmol) and a drop of TMS in an NMR tube. The tube was sealed

~~cally checked for the completion of the reaction. The Hg droplet which collected~~ on the bottom of the tube was separated by decantation. Toluene formed in the reaction was separated by low-temperature distillation at 0.1 mmHg. For variable temperature NMR studies the tube was sealed under vacuum.

Acknowledgment

References

1 A.L. Rheingold in A.L. Rheingold (Ed.), Homoatomic Rings and Chains of Main-Group Elements, Elsevier, Amsterdam, 1977, p. 385.

2 A.L. Rheingold and J.M. Bellama, J. Organometal. Chem., 102 (1975) 437, 445.
3 P.S. Elmes, S. Middleton, and B.O. West, Aust. J. Chem., 23 (1970) 1559.
4 Pseudorotation, a circumannular, vertical atomic displacement, leads to a three-line (2 : 2 : 1) NMR pattern if NMR-rapid and a five-line pattern if NMR-slow.
5 A. Quick and R. Adams, J. Amer. Chem. Soc., 44 (1922) 810.
6 A.L. Rheingold and P. Choudhury, J. Organometal. Chem., 128 (1977) 155.
7 L.H. Krannich and H.H. Sisler, Inorg. Chem., 8 (1969) 1032.
8 J.W. Emsley, J. Feeney and L.H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Pergamon, Oxford, 1966, Vol. 2, p. 676. A referee has suggested that electronegativity considerations may, instead, be the dominant factor.
9 A.L. Rheingold, unpublished results.
10 H.J. Burns and J. Waser, J. Amer. Chem. Soc., 79 (1957) 859.
11 J. Waser and V. Schomaker, J. Amer. Chem. Soc., 67 (1949) 2014.
12 Similar concentration dependencies have been previously observed in PMCA. C.L. Watkins, L.K. Krannich and H.H. Sisler, Inorg. Chem., 8 (1969) 385.
13 A.I. Vogel, Textbook of Practical Organic Chemistry, Wiley, New York, 1966.