Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

SYNTHESIS OF ORGANOLEAD COMPOUNDS
II*. PREPARATION AND PROPERTIES OF 5-PLUMBASPIRO[4.4]-NONANE

KENNETH C. WILLIAMS
Ethyl Corporation, Baton Rouge, Louisiana 70821 (U.S.A.)

(Received May 9th, 1969)

Infrared adsorption data on heterocyclic compounds incorporating one or more of the main Group IV elements have shown that correlations exist that are helpful in their identification[2,3,4]. Bajer and Post[2] have prepared five and six-membered spirocyclic compounds of silicon, germanium and tin, but the corresponding lead compounds were not prepared. Recently Juenge and Jack[5] first reported the successful synthesis of a spirocyclic lead compound. They prepared 5-plumbaspiro[4.4]-nonane from reaction of butane-1,4-dimagnesium bromide with a lead(IV)compound, ammonium hexachloroplumbate. This has prompted us to report the preparation of 5-plumbaspiro[4.4]nonane from reaction of lead chloride and the di-Grignard reagent of 1,4-dichlorobutane.

Yields of up to 65% were obtained from the reaction under anhydrous work-up conditions. In experiments where the excess of Grignard reagent was hydrolyzed prior to work-up, only white polymeric materials which slowly turned yellow on standing were isolated. This phenomenon probably accounts for the failure of Juenge and Jack to obtain the spirolead compound from lead(II) chloride. Several attempts were made to prepare the compound by reaction of the di-Grignard reagent with lead tetraacetate, but under all conditions tested only a viscous, polymeric material was obtained.

The 5-membered spirocyclic lead compound is a dense ($d^{25} = 2.025$ g/ml), colorless liquid which boils at 63–67° (1 mm) without decomposition, but upon standing it slowly decomposes as evidenced by formation of yellow polymeric solids. The proton magnetic resonance spectrum consisted of two multiplets centered at τ 7.98 and 8.48; the peak areas were in the ratio of 1/1, as expected for the proposed compound. Lead coupling (21.11% natural abundance of ^{207}Pb) was observed (J 136.0 Hz) centered around the resonance at τ 7.98. We have tentatively assigned the downfield resonance to the β protons and the highfield resonance to the α protons. This assignment is based on the observation that lead coupling with β protons in

---

[*] For Part I see ref. 1.

tetraethyllead and various substituted ethyllead compounds is always larger than for α protons[6,7]. In the spectrum of 5-plumbaspiro[4.4]nonane no coupling larger than J 136.0 Hz was observed, and due to the multiplet structure of the resonances, a coupling constant of 30 Hz or less could not have been detected. In various ethyllead compounds the lead coupling constants with α protons varies from 41 to 53 Hz, whereas, with β protons the coupling ranges from 125 to 150 Hz. The lead coupling constants for α protons in several substituted neopentyllead compounds are in the range of 28 to 42 Hz[8].

Table 1 lists the mass-spectral data for 5-plumbaspiro[4.4]nonane. The spectrum shows a relatively intense parent peak as compared to what usually is observed for tetraalkyllead compounds[9,10]. This observation is consistent with the generalization that cyclic structures produce more abundant parent molecular ions. No peaks having a mass greater than the molecular weight of the compound were detected.

The infrared absorption data are presented in Table 2. The spectrum shows bands at 1078 and 1008 cm^{-1} which are particularly characteristic of five-membered rings[2]. The strong bands at 508 and 408 cm^{-1} probably are vibrations associated with Pb–CH_2 stretching[11,12].

TABLE 1

MASS-SPECTRAL DATA. ION ABUNDANCE RELATIVE TO TOTAL LEAD-CONTAINING IONS

Ion$^+$	Relative abundance
PbC_6H_{16}	11.8
PbC_6H_{12}	0.2
PbC_4H_8	9.2
PbC_2H_4	9.2
$PbCH_2$	0.7
HPb	4.3
Pb	64.5

TABLE 2

TABULATION OF INFRARED DATA FOR 5-PLUMBASPIRO[4.4]NONANE

2880 s	1310 m	887 w
2695 w	1247 m	855 m
2080 w	1220 s	828 w
2030 w	1173 s	738 s
1960 w	1078 s	726 s
1905 w	1044 m	695 w
1588 w	1008 s	508 s
1440 s	948 m	408 s
1408 w	905 w	

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was distilled from lithium aluminum hydride before use. The proton magnetic resonance spectrum was measured in a solution of carbon tetrachloride (10%) using a

Varian Associates A-60 spectrometer. Infrared spectra were determined in KBr discs on a Perkin–Elmer Model 21 and Perkin–Elmer Model 137KBr spectrometers; the mass spectrum was determined using a Hitachi Perkin–Elmer RMU-6E mass spectrometer, operating at an ionizing current of 10.5 μA and an ionization energy of 70 eV. The inlet and ionization chamber temperatures were 125° and 150° respectively.

5-Plumbaspiro[4.4]*nonane*

The di-Grignard reagent of 1,4-dichlorobutane was prepared from 15.2 g (0.12 mole) of the dichloride and an excess of magnesium metal in 600 ml of tetrahydrofuran. After the exothermic reaction subsided, the di-Grignard solution was heated at reflux for 30 min to insure complete reaction. To the freshly prepared and filtered di-Grignard reagent was added 27.8 g (0.1 mole) of lead(II) chloride while the temperature was maintained at 25–30°. Lead metal separated and a yellow solution was obtained which became colorless when heated at reflux for 15 min. After tetrahydrofuran had been removed by distillation at reduced pressure, the residue was extracted twice with 200 ml portions of pentane. Evaporation of the pentane gave a crude product which was vacuum-distilled to give 10.5 g (65.8%) of colorless liquid boiling at 63–64° (1 mm). (Found: Pb, 64.9. (average of three analyses). $C_8H_{16}Pb$ calcd.: Pb, 64.87%.)

ACKNOWLEDGEMENT

Acknowledgement is made to Mr. S. R. Henderson for the lead analysis, Mr. J. B. Chidester for the mass spectrum and Dr. D. W. Imhoff for the infrared and proton magnetic resonance spectra.

REFERENCES

1 K. C. Williams, *J. Org. Chem.*, 32 (1967) 4062.
2 F. J. Bajer and H. W. Post, *J. Organometal. Chem.*, 11 (1968) 187.
3 E. C. Juenge and S. Gray, *J. Organometal. Chem.*, 10 (1967) 465.
4 F. J. Bajer and H. W. Post, *J. Org. Chem.*, 27 (1962) 1422.
5 E. C. Juenge and H. E. Jack, *Midwest Regional American Chemical Society Meeting*, Manhattan, Kansas, November 1, 1968.
6 M. L. Maddox, S. L. Stafford and H. D. Kaesz, *Advan. Organometal. Chem.*, 3 (1965) 1.
7 K. C. Williams, unpublished data.
8 G. Singh, *J. Organometal. Chem.*, 11 (1968) 133.
9 J. J. de Ridder and G. Dijkstra, *Rec. Trav. Chim.*, Pays-Bas, 86 (1967) 737.
10 D. B. Chambers, F. Glockling and M. Weston, *J. Chem. Soc.*, (1967) 1759.
11 E. R. Lippincott and M. C. Tobin, *J. Amer. Chem. Soc.*, 75 (1953) 4141.
12 R. J. H. Clark, A. G. Davies and R. J. Puddephatt, *J. Amer. Chem. Soc.*, 90 (1968) 923.