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

SYNTHESIS AND POLYMERIZATION OF 5-PLUMBASPIRO[4.4]NONANE AND STUDY OF RELATED PLUMBACYCLOPENTANES AND PLUMBACYCLOHEXANES

ERIC C. JUENGE AND H. EUGENE JACK
Kansas State College of Pittsburg, Pittsburg, Kansas 66762 (U.S.A.)

(Received August 1st, 1969; in revised form October 28th, 1969)

SUMMARY

5-Plumbaspiro[4.4]nonane has been prepared by the Grignard procedure in 9% yield and its IR and NMR spectra have been studied and compared with those of related plumbacyclopentanes and plumbacyclohexanes.

Several investigations of spirocyclic compounds of Group IVA have been reported[1,2,3] but analogs of lead have not been prepared. As part of our study[4,5], we report the synthesis, polymerization and spectral properties of 5-plumbaspiro-[4.4]nonane including a study of related plumbacyclopentanes and plumbacyclohexanes. This spirocyclic compound was prepared by reaction of tetramethylenedimagnesium dibromide with potassium hexachloroplumbate in diethyl ether. In several runs, ammonium hexachloroplumbate(IV) was treated with tetramethylenedimagnesium dibromide in diethyl ether. The resulting yellow solutions gave indication of the presence of an organolead compound on treatment with alcoholic silver nitrate. However, thick yellow untractable oils formed, which tended to polymerize.

The above procedure was used in an attempted preparation of 6-plumbaspiro-[5.5]undecane by reaction of pentamethylenedimagnesium bromide with potassium hexachloroplumbate(IV). This reaction resulted in the formation of 1,1-dipentylplumbacyclohexane, probably by incomplete ring closure. A similar incomplete ring closure has been reported by Mazerolles[2] for the germanium analog.

Infrared spectral data for 5-plumbaspiro[4.4]nonane and 1,1-dipentylplumbacyclohexane are presented in Table 1. The spectra of both of these compounds appear to be consistent with those expected for five- and six-membered heterocyclic compounds of Group IV A. Five-membered heterocyclic compounds of silicon, germanium and tin have been shown[5] to have characteristic absorptions centered at approximately 1080 and 1025 cm^{-1}, while absorptions centered at 990 and 910 cm^{-1} have been reported[6,7] to be characteristic of six-membered heterocyclic compounds of Group IV A. 5-Plumbaspiro[4.4]nonane shows absorptions centered at 1090, 1020, 962 and 911 cm^{-1} and 1,1-dipentylplumbacyclohexane has absorptions centered at 1093, 971 and 911 cm^{-1}. Comparison of these values with those given above for related five- and six-membered heterocyclic compounds of Group IV A indicates that determination of the ring size of cycloplumbanes from characteristic absorptions may be

TABLE 1

TABULATION OF INFRARED DATA (cm^{-1})

5-Plumbaspiro[4.4]nonane			1.1-Dipentylplumbacyclohexane		
3000 m	1330 w	1018 m	2967 s	1429 w	1136 w
2959 s	1246 w	962 m	2945 s	1382 w	1089 w
2945 s	1232 m	911 w	2900 s	1345 m	1093 w
2860 s	1190 m	862 m	2865 s	1280 w	971 m
1449 m	1090 w	838 w	1475 m	1230 w	911 m
1445 w	1062 w	746 s	1464 m	1190 w	725 s
1418 w	1020 w	734 s	1451 m	1163 w	

more difficult. The spectra of both of these compounds also show a strong absorption in the region 725–735 cm^{-1}, which has been reported to be present in other cyclic lead compounds[4].

In an attempt to correlate spectra with structure, the nuclear magnetic resonance spectrum of 5-plumbaspiro[4.4]nonane[5], is presented here along with spectra of 1,1-diethylplumbacyclopentane, 1,1-diethylplumbacyclohexane, and 1,1-dipentylplumbacyclohexane. Narasimhan and Rogers[8] have analyzed the spectra of several organometallic ethyl compounds as A_3B_2 systems. The Dailey and Shoolery[9] equation has been shown by Baker[10] to explain the NMR spectrum of tetraethyllead. The spectra of the six-membered cyclic plumbanes resemble closely the spectra of silacyclohexanes studied by Benkeser, Smith and Noe[11]. The spectra for the five-membered cyclic plumbanes including the spirane, appear to show close correlation with the ring methylene absorptions shown in the Sadtler Reference Spectra of tetrahydrothiophene-1,1-dioxide and tetrahydrofuran.

The spectra of 5-plumbaspiro[4.4]nonane has two major absorption multiplets at 1.61 and 2.11 ppm. These absorptions are tentatively attributed to the α- and β-methylenes, respectively. The ^{207}Pb isotope splits the multiplet at 2.11 ppm (β-methylene) into a satellite doublet, J 134.0 Hz. The ^{207}Pb isotope is also observed to split the methylene absorption at 1.61 ppm (α-methylene) into a satellite doublet, J 62.0 Hz. The spectrum of tetraethyllead shows a single large peak due to the presence of the lead atom which causes the methylene proton resonance to shift upfield and become identical with that of the methyl proton resonance. In the spirane, the methylene groups differ only by the attachment of the lead atom, so that the α-methylene protons show a chemical shift upfield relative to the β-methylene protons. This is further supported by the fact that γ-methylene proton resonance occurs together with β-methylene proton resonance and occurs downfield from the α-methylene resonance in 1,1-diethylplumbacyclohexane. This assignment of α- and β-methylene proton resonances is also consistent with the relative coupling constants observed for α- and β-protons in tetraethyllead[10].

The spectrum of 1,1-diethylplumbacyclopentane has absorption multiplets at 1.32 ppm and 1.88 ppm which may be attributed respectively to the α- and β-methylenes of the heterocyclic ring. A central multiplet in the region 1.43–1.58 ppm is attributed to the methyl and methylene protons of the ethyl groups. This multiplet, consisting essentially of four peaks, is resolvable into a very complex group of peaks upon expansion of the sweep width. As previously mentioned, in tetraethyllead the protons of the methyl and methylene groups have been shown to have practically the same chemical shifts within 1 Hz[10]. The ^{207}Pb isotope splits the methyl protons of the ethyl groups into satellite triplets, J 136.0 Hz.

As expected, the nuclear magnetic resonance spectrum for 1,1-diethylplumbacyclohexane appears more complex than the spectra for the plumbacyclopentane compounds. A complex absorption with a chemical shift centered at 1.80 ppm is attributed to β- and γ-methylene protons of the ring. Ethyl proton absorptions, along with an α-methylene ring proton absorptions appear as a very complex pattern in the region 1.04–1.64 ppm. Satellite splitting of the β-methylene peak at 1.80 ppm, attributed to the ^{207}Pb isotope occurs, J 128.0 Hz. Two satellite triplets, J 134.0 Hz, are attributed to the ^{207}Pb isotope splitting the methyl protons of the ethyl groups, analogous to that observed for tetraethyllead[10].

1,1-Dipentylplumbacyclohexane has a complex absorption centered at 1.78 ppm, which is tentatively attributed to the β- and γ-protons of the ring methylenes. A much larger multiplet centered at 1.55 ppm is tentatively assigned to the β-, γ- and δ-methylenes of the side chains. A triplet at 0.93 ppm is attributed to the terminal methyl groups. The peak areas for these compounds are consistent with that expected and further work to generate theoretical spectra is now in progress.

The 5-plumbaspiro[4.4]nonane can be polymerized by heating at 120° for several hours, or by storage at 0° for several months, or by refluxing in benzene with a free radical polymerization catalyst. Under the conditions described above, only the spirane underwent polymerization, the plumbacyclopentane and the plumbacyclohexane did not.

EXPERIMENTAL

1,1-Diethylplumbacyclopentane was prepared according to the procedure of Juenge and Gray[4]. Its purity for spectra analysis was determined by gas–liquid chromatography. 1,1-Diethylplumbacyclohexane was prepared by a modification of the procedure of Grüttner[12]. The NMR spectra data presented in this paper was obtained by the use of a Varian HA 100 nuclear magnetic resonance spectrometer. Only freshly distilled samples were used. Tetramethylsilane was the internal standard. The samples were analyzed as 30%–40% solutions, by volume, in chloroform. Infrared spectra were obtained on neat films by the use of a Perkin–Elmer Model 337 spectrophotometer and are uncorrected. All reactions were carried out under inert atmosphere.

5-Plumbaspiro[4.4]*nonane*

Tetramethylenedimagnesium dibromide was prepared by the reaction of 162 g (0.75 mole) of 1,4-dibromobutane with 36.4 g (1.50 mole) of magnesium in 500 ml of dry ether. The ethereal solution of the dihalide was added dropwise to the magnesium in a two liter flask equipped with a pressure equalized dropping funnel, stirrer, and a reflux condenser. After the reaction started, external cooling was applied, and the ethereal solution of dihalide was added at a sufficient rate to maintain reflux. The addition of the halide was completed in 45 min, and the ethereal solution was stirred for an additional hour. The reaction mixture then was diluted with 500 ml of dry ether. Potassium hexachloroplumbate(IV), (187 g, 0.380 mole) was added over 2 h with vigorous stirring at a sufficient rate to maintain reflux, and the contents of the flask were refluxed for three more hours. The reaction mixture was cooled and hydrolyzed by stirring and dropwise addition of 500 ml of water. The pale-yellow ethereal layer was separated, dried over $CaSO_4$ for several hours, and the ether was removed by distillation through a two-feet column. The thick, oily residue was transferred to a 100 ml flask immersed to its neck in an oil bath. The material was flash distilled under vacuum (0.2 mm) with the oil bath temperature at 120° for a one-half hour period. The distillate was redistilled through a one-foot Vigreux column yielding 11 g of crude product (9.2%), b.p. 41–44°/0.02 mm. Refractionation through a one-foot column packed with glass beads gave 7.90 g of 5-plumbaspiro[4.4]nonane, b.p. 41–43°/0.02 mm. Some decomposition was observed during each of the distillations. (Found: C, 30.15; H, 5.04. $C_8H_{16}Pb$ calcd.: C, 30.24; H, 5.11%.)

1,1-*Dipentylplumbacyclohexane*

Pentamethylenedimagnesium dibromide was prepared from (149.5 g, 0.650 mole) of 1,5-dibromopentane and (31.6 g, 1.30 mole) of magnesium metal in 500 ml of dry ether. The reaction was carried out by the same procedure used for the preparation of the 5-plumbaspiro[4.4]nonane. After completion of the reaction, an additional 500 ml of ether was added. Potassium hexachloroplumbate(IV), (124.5 g, 0.250 mole), was added in 45 min with vigorous stirring at a sufficient rate to maintain reflux. The work up was identical with that given for the spirane. After refractionation, 7.2 g of product (7.8%) was obtained as a colorless liquid, b.p. 86–87°/0.05 mm. (Found: C, 43.27, 43.10; H, 7.74, 7.53; mol.wt., 414. $C_{15}H_{32}Pb$ calcd.: C, 42.96; H, 7.14%; mol.wt., 420.)

Thermal polymerization 5-plumbaspiro[4.4]*nonane*

5-Plumbaspiro[4.4]nonane (20 g) was heated at 120° for 3 h in the absence of air. The pale yellow solid which separated from the liquid was collected and washed with ether to remove the unreacted spirane to give 4.0 g of the product. [Found: C, 30.15; H, 5.04. $(C_8H_{16}Pb)_x$ calcd.: C, 30.24; H, 5.11%.)

Polymerization of 5-plumbaspiro[4.4]*nonane at* 0°

A clear transparent polymer formed after storage of the spirane at 0° for a ten-months period. This material was triturated with benzene, centrifuged and then collected. This product produced a black precipitate on treatment with alcoholic silver nitrate indicating the presence of a tetraalkyllead structure. [Found: C, 30.24; H, 5.04. $(C_8H_{16}Pb)_x$ calcd.: C, 30.24; H, 5.11%.)

Polymerization of 5-plumbaspiro[4.4]*nonane under free radical catalysis*

Solutions containing 0.80 g of 1,1-diethylplumbacyclopentane, 1,1-dipentylplumbacyclohexane and 5-plumbaspiro[4.4]nonane were refluxed with 10 ml benzene and 0.01 g of benzoyl peroxide. The spirane showed some precipitate formation in 2 h. Each of the three reaction mixtures was refluxed for 15 h. Only in the case of the spirane was an appreciable amount of the polymer (0.43 g) obtained. This product is insoluble in common organic solvents including dimethyl sulfoxide and dimethylformamide. A black precipitate was formed slowly from the product on treatment with alcoholic silver nitrate. (Found: C, 29.97; H, 4.92. $(C_8H_{16}Pb)_x$ calcd.: C, 30.24; H, 5.11%.)

ACKNOWLEDGEMENT

This investigation was supported in part by Public Health Service Research Grant No. UI-4 00204 from the National Center for Urban and Industrial Health and in part by the National Science Foundation Undergraduate Participation Program. Acknowledgement is also made to R. Briden and J. Ernst for their assistance in the proton magnetic resonance work.

REFERENCES

1 R. West, *J. Amer. Chem. Soc.*, 76 (1954) 6012.
2 P. Mazerolles, *Bull. Soc. Chim. Fr.*, (1962) 1907
3 F. J. Bajer and H. W. Post, *J. Organometal. Chem.*, 11 (1968) 187
4 E. C. Juenge and S. Gray, *J. Organometal. Chem.*, 10 (1967) 465.
5 E. C. Juenge and H. E. Jack, *Midwest Regional A.C.S. Meeting*, Manhattan, Kansas, Oct. 31, 1968.
6 G. D. Oshesky and F. T. Bentley, *J. Amer. Chem. Soc.*, 79 (1957) 2057
7 F. J. Bajer and H. W. Post, *J. Org. Chem.*, 27 (1962) 1422.
8 P. T. Narasimhan and M. T. Rogers, *J. Amer. Chem. Soc.*, 82 (1960) 5983.
9 B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, 77 (1955) 3977.
10 E. B. Baker, *J. Chem. Phys.*, 26 (1957) 960.
11 R. A. Benkeser, S. D. Smith and J. L. Noe, *J. Org. Chem.*, 33 (1968) 597.
12 G. Grüttner, *Ber.*, 47 (1914) 3257.