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SYNTHESIS AND REACTIVITY OF MONO- AND TETRA-1-ADAMANTYL DERIVATIVES OF SILICON, GERMANIUM, TIN AND TITANIUM

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SUMMARY

New 1-adamantyl (Ad) derivatives of silicon, germanium, tin and titanium have been synthesised by reaction of organometal alkalis with 1-haloadamantane and also by a Wurtz–Fittig reaction. Me_3SnAd and Ph_3SnAd are reactive towards electrophilic attack but the tetraadamantyl derivatives of the above elements are remarkably inert. The results indicate that the Wurtz reaction is at least in part an electron-transfer process.

INTRODUCTION

Although the chemistry of adamantane[1] (tricyclo[3.3.1.1^{3,7}]decane) and its non metallic derivatives is now being explored in depth, its organometallic derivatives have received scant attention. This is somewhat surprising since the rigidity of the adamantyl framework would simplify many of the interpretations of kinetic data for electrophilic substitution reactions at the bridgehead carbon. Winstein and Traylor[2] provided the first evidence that such substitution processes are not especially slow (as is the case in nucleophilic substitution) in their study of the cleavage of 4-camphyl-mercury derivatives at the bicyclo [2.2.1]-heptyl bridgehead. Wittig and co-workers[3,4] were able to prepare 1-triptycenyl-lithium by a metal/halogen exchange between 1-bromotriptycene and BuLi and succeeded in synthesising a number of new bridgehead compounds of which di-1-triptycenylmercury is notable in view of its extraordinarily high melting point.

The first report of bridgehead organometallic derivatives of adamantane was that of Lansbury and Sidler[5] who synthesised the 1-lithio derivative by metal/halogen exchange. More recently the reaction of 1-bromoadamantane with trimethyltin derivatives of the alkali metals has been reported independently by two sets of workers[6,7] and Goh and Goh[8] have synthesised 1-adamantylpentacyanocobaltate(III) containing a cobalt–carbon σ bond. The present paper deals with the preparation and reactivity of some new bridgehead adamantyl derivatives of silicon, germanium, tin and titanium.

DISCUSSION AND RESULTS

1-Adamantyltrimethyltin was formed in good yield (65%) from 1-bromoadamantane and trimethyltinsodium in liquid ammonia but the corresponding reaction with triphenyltinsodium resulted in high yields of hexaphenyldistannane and biadamantane. There are two pricipal reaction routes:

$$R_3SnNa + BrR' \rightarrow R_3SnR' + NaBr \tag{1}$$

$$\left.\begin{aligned} &R_3SnNa + BrR' \rightarrow R_3SnBr + R'Na \\ &R_3SnNa + BrSnR_3 \rightarrow R_3SnSnR_3 + NaBr \\ &R'Na + BrR' \rightarrow R'_2 + NaBr \end{aligned}\right\} \tag{2}$$

There is evidence that reaction (1) proceeds with dominant inversion of configuration in polar solvents, but that retention of configuration occurs in less polar media[6,7,9]. In each case it is assumed that the reactions are bimolecular. For the reactions with 1-bromoadamantane, inversion of configuration is precluded and the reaction of the trimethyltin anion (or ion pair) does not appear unusually slow and is certainly much faster than the competing coupling reaction (viewed by Traylor as an S_N2 reaction on the halogen[6]). The latter reaction was found to be dominant in the attempted preparation of Ph_3SnAd, Me_2SnAd_2 and Ph_2SnAd_2 (Ad = 1-adamantyl). Thus it seemed likely that the reaction was under steric control. It was very surprising therefore when tetraadamantyltin was obtained in 20% yield from a Wurtz reaction between stannic choloride and both 1-chloro- and 1-bromoadamantane in cyclohexane. In addition 30% yields of 1-adamantyltriphenyltin were obtained by this method. The mechanism of the Wurtz reaction is still in some doubt. Earlier work suggested an ionic mechanism[10,11] but recently evidence of radical species has been found[12], admittedly not under the usual reaction conditions. If the mechanism were ionic then the terminal stage of the Wurtz reaction under consideration, which is presumably

$$Ad_3SnCl + NaAd \rightarrow Ad_4Sn + NaCl \tag{3}$$

would be prohibitively slow compared with biadamantane formation due to the much greater steric hindrance of the Ad_3Sn group compared with Ph_3Sn though, of course, electronic factors will also contribute. Nevertheless it is clear from evidence to be presented later that adamantyl groups protect the tin–carbon bond very effectively from electrophilic attack. This, then, suggests that the ionic mechanism is not operative in this instance, and that the alternative radical process must be invoked, involving electron transfer from the sodium atom to the R_3SnX and AdX species.

$$R_3SnX + \cdot Na \rightarrow R_3Sn\cdot + NaX \tag{4}$$

$$AdX + \cdot Na \rightarrow \cdot Ad + NaX \tag{5}$$

$$R_3Sn\cdot + \cdot Ad \rightarrow R_3SnAd \tag{6}$$

$$R_3Sn\cdot + \cdot SnR_3 \rightarrow R_3SnSnR_3 \tag{7}$$

$$Ad\cdot + \cdot Ad \rightarrow Ad_2 \tag{8}$$

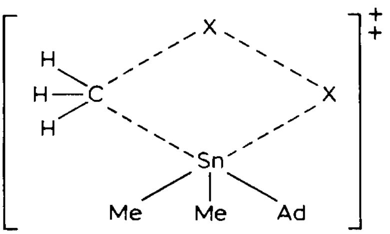
In all the Wurtz reactions performed in this investigation the unwanted couplings, (7) and (8), occurred to a greater or lesser degree. Support for the electron transfer mechanism comes from recent evidence that the adamantyl radical itself is fairly long lived[13] and shows some selectivity in its reactions.

It is significant that under "ionic" conditions no Ph_3SnAd was formed but under Wurtz conditions (refluxing cyclohexane) an appreciable yield was obtained. This may well be due to the different steric requirements of the radical process.

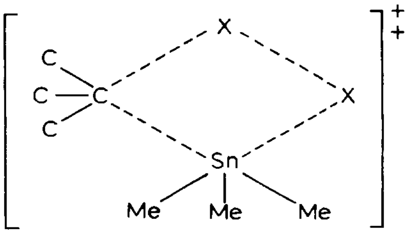
The Wurtz reaction was used to synthesise other tetraadamantyl derivatives in yields given in parentheses, Ad_4Ge (26), Ad_4Si (18), Ad_4Ti (18).

Reactivities of 1-*adamantyl derivatives* [*chemical shifts of protons* δ (*ppm*), *appear in parentheses*]

Me_3SnAd reacted with bromine in $CDCl_3$ (0.1 *M* in each reagent) at rates comparable with that of Me_4Sn to give a solution whose NMR showed the following resonances; MeBr (2.64 singlet), AdBr (2.35 doublet, 1.72 doublet), $AdSn(Br)Me_2$ (2.07 mult., 1.83 mult., 0.57 singlet), Me_3SnBr (0.75 singlet). By integrating the tin methyl resonances it was possible to estimate that 48 % Me–Sn bond fission had occurred compared with the statistical value of 75 %. Iododestannylation resulted in 66 % Me–Sn bond fission. These results are in accord with a four-centre transition state[14] (S_F):



(I)



(II)

Nucleophilic assistance being less sterically hindered than electrophilic attack on carbon due to the difference in bond lengths between Sn–X and C–X. Thus transition state (I) is favoured as the size of X increased.

Me_3SnAd reacted with $HgCl_2$ in DMSO-d_6 to give exclusively Me–C bond fission as judged from the appearance of MeHgCl (1.02) and $Me_2Sn(Cl)Ad$ (0.50) and the absence of Me_3SnCl (0.61) signals in the NMR spectrum of product solutions. Since $HgCl_2$ and I_2 have comparable steric size in terms of S_F transition state interactions it would seem that the dominance of C–Me bond fission in the mercury–tin exchange results from a change to a more open ionic transition state structure. Ph_3SnAd reacted with bromine in $CDCl_3$ (0.1 *M* in each reagent) instantaneously with exclusive phenyl–tin bond cleavage.

The tetraadamantyl derivatives were all extremely unreactive. Ad_4Sn showed little or no reaction with bromine (0.1 *M*) over a period of weeks, and was unaffected by $HgCl_2$ in refluxing MeCN (1 day). Even more striking was the lack of reactivity of the titanium analogue. Titanium tetraalkyls are among the most reactive of organometal systems[15] yet in this instance the compound proved difficult to decompose with $HNO_3/HF/H_2O_2$ mixtures at 170° when analysing for the metal[16]. The four adamantyl groups around the central metal atom provide quite remarkable insulation against attack by polar reagents.

The melting points of the derivatives all lie above 200°. The compounds are all highly soluble in non-polar solvents and virtually insoluble in solvents such as

MeOH and DMSO. The PMR spectra show interesting trends. It is possible in the case of tin to differentiate between proton systems associated with C2 (C8 and C9), C3 (C5 and C7) and C4 (C6 and C10), whereas for silicon the spectrum is very similar that of biadamantane. This effect cannot be due to the slight electronegativity difference between Si and Sn but probably reflects the different anistropy of the Si–C and Sn–C bonds. A more detailed examination of ^{13}C and mass spectra of these new compounds will appear at a later date.

The tetraadamantyl derivatives of silicon and tin may well find use as references in ^{29}Si and ^{119}Sn NMR spectroscopy. They have the advantage that their chemical shifts should be largely solvent independent in view of the marked insulation of the central metal atom.

Infrared spectra of tetraadamantyl derivatives

The IR spectra of the MAd_4 derivatives (0.025 *M* in CCl_4) are very similar to those of biadamantane except for certain bands in the 1500–900 cm^{-1} region. All show strong absorptions at 2930 and 2855 cm^{-1} due to asymmetric and symmetric CH_2 stretching modes respectively, and also a strong CH stretching mode at 2910 cm^{-1}. In addition, weak but characteristic bands appear near 2650 cm^{-1} in all the spectra and have been attributed[17] to a combination of CH and CH_2 modes at 1350 and 1310 cm^{-1}.

The spectra of the silicon and titanium derivatives are very similar to that of biadamantane but of greater intensity. Significant differences occur however for germanium and tin, with the appearance of a new band near 1300 cm^{-1}. Similar bands have been observed for other 1-adamantyl derivatives (OH, F, Cl, Br, CH_2OH). All the spectra show skeletal vibrations at 1105, 1038 and 968 cm^{-1}, of variable intensity. CH_2 scissoring modes appear at 1452 cm^{-1}, but there is still some doubt about the assignment of the characteristic absorptions at 1358 and 1347 cm^{-1} and at 1310 cm^{-1} which may be due to either CH deformation or a CH_2 wagging mode.

EXPERIMENTAL

1-Chloro[18]-and 1-bromoadamantane[19] were prepared by previously reported methods. Biadamantane was obtained by a Wurtz coupling reaction in boiling xylene[20].

Preparation of 1-*adamantyltrimethyltin*

Me_4Sn (10 g, 0.0558 mole) was added dropwise to a stirred solution of sodium (2.58 g, 0.112 g-atom) in liquid ammonia (50 ml) under dry argon excluding moisture and atmospheric carbon dioxide by calcium chloride and soda lime guard tubes. After all the Me_4Sn had been added, the original blue colour of the solution changed to pale yellow with a white precipitate. The mixture was stirred for a further $\frac{1}{2}$h and then a solution of 1-bromoadamantane (10 g, 0.0465 mole) in dry 40–60° pet. ether (50 ml) was added. The mixture was stirred at room temp. overnight and any excess Me_3SnNa decomposed with saturated NH_4Cl. The mixture was extracted with 3×50 ml 40–60° pet. ether and the extracts dried over $CaCl_2$. After removing the solvent, a white solid was obtained which was crystallised from methanol to give Me_3SnAd (9.0 g 65%), m.p. 57–58°. (Found: C, 52.3; H, 8.05. $C_{13}H_{24}Sn$ calcd.: C, 52.2; H, 7.87%.) The PMR spectrum in CCl_4 showed resonances at 2.02–1.82 ppm (mult., adamantyl protons) and 0.07 ppm, the latter possessing attendant tin satellites, $J(^{119}Sn\text{-}H)$ 55.2 Hz, $J(^{117}Sn\text{-}H)$ 53.4 Hz. From integration the adamantyl proton/tin methyl proton ratio was 1.74/1. ^{13}C chemical shifts (ppm from CS_2) were as follows, the assignments being made by reference to values obtained for adamantane itself[21]. (For numbering the adamantane ring system see ref. 1.) C2, C8, C9 (150.5); C3, C5, C7 (163.2); C4, C6, C10 (154.7); Me_3Sn (206.5). No resonance was found for the unique C1 but the corresponding atom in the norbornyl system has a chemical shift of 154.9 ppm which is very close to the observed C4, C6, C10 values and the latter may well mask it. The compound decomposed after 24 h in CCl_4, but appeared to be quite stable in cyclohexane. The IR spectrum run on fresh CCl_4 solutions showed the following absorptions: 2975 s, 2890 vs, 2845 s, 2835 s, 2675 w, 2655 w, 2644 vw, 2610 vw, 2350 w, 1400 vw, 1342 s, 1300 w, 1249 m, 1185 s, 1175 w, 1102 m, 1049 m, 1039 vw, 971 s, 960 m, 925 w, 823 m, 760 vs, 700 m cm^{-1}.

Preparation of 1-adamantyltriphenyltin and related compounds

The above method for the triphenyl analogue resulted only in the formation of $Ph_3SnSnPh_3$ and biadamantane, and a Wurtz reaction was therefore employed. Ph_3SnCl (7.71 g, 0.02 mole) and 1-chloroadamantane (3.40, 0.02 mole) were dissolved in a minimum volume of hot dry cyclohexane (ca. 20 ml) and added rapidly to a refluxing mixture of sodium (0.92 g, 0.04 g-atom) and dry cyclohexane (ca. 5 ml) under dry nitrogen with the exclusion of moisture. The mixture was then refluxed for 6 h, filtered hot and the residue washed with a little dry cyclohexane. On standing overnight crystals of $Ph_3SnSnPh_3$ appeared (1.4 g). These were filtered off and the filtrate pumped to dryness. The residue was recrystallised from pet. ether 80–100° to give 1.8 g (19%) 1-adamantyltriphenyltin (nc), m.p. 154°. (Found: C, 69.1; H, 6.07; Sn, 24.5. $C_{28}H_{30}Sn$ calcd.: C, 69.3; H, 6.19; Sn, 24.5%.) The PMR spectrum showed aromatic resonances centred at 7.36 ppm and two broad singlets of the adamantyl system at 2.33 and 1.88 ppm. The compound was stable in CCl_4, and showed the following major IR absorptions in this solvent 3070 m, 3050 m, 3020 w, 2990 w, 2905 vs, 2850 s, 1482 m, 1450 m, 1431 vs, 1344 m, 1332 vw, 1300 m, 1250 vw, 1191 vw, 1177 vw, 1100 vw, 1075 vs, 1044 m, 1024 mw, 998 mw, 960 w, 924 vw, 699 vs cm^{-1}. Other methods of synthesis were tried, the most notable being an attempted decarboxylation of $Ph_3SnOCOAd$[22] but on heating at 300° no CO_2 was evolved and the product showed that some loss of phenyl groups had occurred.

Attempts to prepare the trimethylsilyl analogue via the Wurtz method resulted in unwanted coupling products.

Preparation of tetraadamantyl derivatives

These compounds were synthesised by a Wurtz reaction similar to the one described above except that both reagents were soluble in cold cyclohexane and the reaction period was extended to 18 h. Concentrations of the appropriate tetrachloride were kept at 0.3–0.5 *M* in accordance with the findings of Van der Kerk and Luijten[23]. and a 4/1 mole ratio of ClAd to MCl_4 was used. There was no evidence of any prior reaction between the tetrachloride and 1-chloroadamantane. In each case appreciable quantities of biadamantane were formed. The impurity was removed either by sublimation (1 mm at 100°) or by recrystallisation from CCl_4/ethanol mixtures. The following derivatives were synthesised with yields in parentheses. All m.p.'s were determined in sealed tubes.

(*i*). *Tetra*-1-*adamantylsilane* (18%) (nc), m.p. 255°. (Found: C, 84.7; H, 10.9; Si, 4.6. $C_{40}H_{60}Si$ calcd.: C, 84.5; H, 10.6; Si, 4.9%.) PMR shows broad singlets at 1.97 and 1.62 ppm.

(*ii*). *Tetra*-1-*adamantylgermane* (26%) (nc), m.p. 228°. (Found: C, 78.2; H, 9.9; mol. wt., 593. $C_{40}H_{60}Ge$ calcd.: C, 78.2; H, 9.8%; mol. wt., 613.) PMR shows broad singlets at 1.83 and 1.63 ppm.

(*iii*). *Tetra*-1-*adamantyltin* (20%) (nc), m.p. 242°. (Found: C, 73.1; H, 9.2; Sn, 17.6; mol. wt., 673. $C_{40}H_{60}Sn$ calcd.: C, 73.0; H, 9.1, Sn, 18.0; mol. wt., 658.) PMR shows broad singlets at 2.32, 1.88, and 1.62 ppm.

(*vi*). *Tetra*-1-*adamantyltitanium* (18%) (nc), m.p. 233–235°. (Found: C, 82.1; H, 10.7; Ti, 8.1. $C_{40}H_{60}Ti$ calcd.: C, 81.7; H, 10.3; Ti, 8.1%.) PMR shows broad singlets at 1.97 and 1.62 ppm.

All the tetraadamantyl derivatives were exceedingly soluble in hydrocarbon or chlorinated hydrocarbon solvents and only very slightly soluble in polar solvents such as MeOH, acetone, DMSO. Some difficulty was experienced in removing the last traces of cyclohexane entrained in the derivatives.

Cleavage of 1-*adamantyltrimethyltin by mercuric chloride*

1-Adamantyltrimethyltin (0.30 g, 1.0 mmole) was dissolved in acetone (5 ml) and treated with mercuric chloride (0.27 g, 1.0 mmole) in acetone (2 ml). A white ppt. formed almost immediately. The mixture was allowed to stand at 0° for $\frac{1}{2}$h then filtered to give 0.2 g (63%) 1-adamantyldimethyltin chloride (nc), m.p. 141°. (Found C, 45.0; H, 6.45. $C_{12}H_{21}$ ClSn calcd.: C, 45.1; H, 6.58%.) The PMR spectrum comprised two broad singlets 2.07 and 1.79 ppm from the adamantyl protons, and a sharp singlet at 0.47 ppm with attendant tin satellites, $J(^{119}Sn{-}H)$ 61.5, $J(^{117}Sn{-}H)$ 59.1 Hz, from the tin methyl groups.

Infrared spectra

Routine spectra were run on a Unicam SP 200 instrument. More accurate spectra were recorded in CCl_4 (at 0.025 *M*) on a Perkin Elmer 257 spectrophotometer.

NMR spectra

PMR spectra were obtained using a Varian A60A instrument. ^{13}C work was done in cyclohexane or CCl_4 on a JEOL Co. Ltd. JNM C60 HL instrument.

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REFERENCES

1 R C Fort and P Von R. Schleyer, *Chem. Rev*, 64 (1964) 277
2 S Winstein and T G. Traylor, *J Amer Chem. Soc*, 78 (1956) 2597.
3 G Wittig and U Schollkopf, *Tetrahedron*, 3 (1958) 91
4 G. Wittig and W Tochtermann, *Justus Liebigs Ann Chem.*, 660 (1962) 23
5 P T. Lansbury and J D. Sidler, *Chem Commun*, 16 (1965) 373
6 G S. Koermer, M L Hall and T G Traylor, *J Amer Chem Soc.*, 94 (1972) 7205.
7 H G Kuivila, J L Considine and J D. Kennedy, *J Amer Chem Soc* 94 (1972) 7206

8 S H Goh and L.-Y Goh, *J Orgnometal. Chem*, 43 (1972) 401

9 C H W Jones, R G Jones, P Partington and R M G Roberts, *J Organometal. Chem*, 32 (1971) 201

10 J Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, 2nd Ed., 1962, p 245

11 E LeGoff, S E Ulrich and D B Denney, *J Amer Chem Soc* 80 (1958) 622

12 J F Ganst and R. H Cox, *J Amer Chem Soc*, 92 (1970) 6389

13 I Tabushi, Y Aoyama, S Kojo, J Hamuro and Z Yoshida, *J. Amer Chem Soc*, 94 (1972) 1177

14 M Gielen and J Nasielski, in A. K Sawyer (Ed), *Organotin Compounds*, Vol 3, Marcel Dekker, New York, 1972, p 625

15 R J H. Clark, *The Chemistry of Titanium and Vanadium*, Elsevier, Amsterdam, 1st Ed, 1968, p 230

16 M Hart, personal communication

17 T J. Broxton, L W Deady, M Kendall and R D Topsom, *Appl Spectrosc*, 25 (1971) 600

18 H Stetter, M Schwartz and A. Hirshhorn, *Chem Ber*, 92 (1959) 1629

19 K Gerson, E V. Krumkalns, R L Brindle, F J Marshall and M A Root, *J Med Chem*, 6 (1963) 760

20 H F Reinhardt, *J Org Chem*, 27 (1962), 3258

21 E Lippmaa, T Pehk and J Past, *Eesti, NSV, Tead Akad Toim Fuus Met*, 16 (1967) 345

22 R. H Fish and C. W LeFabre, *Chem Abstr* 70 (1969) 37917a.

23 G J M Van der Kerk and J G A Luijten, *J Appl Chem*, 4 (1954) 301