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SYNTHESIS AND REACTIVITY OF SOME BRIDGEHEAD ORGANOTIN DERIVATIVES OF TRIPTYCENE

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Summary

New organotin derivatives of triptycene are reported. The reactivity of these compounds has been studied semi-quantitatively. In 9-trimethylstannyltriptycene, the tin—triptycene bond is inert to electrophilic substitution and the tin—methyl bonds are much less reactive than the corresponding bonds in 1-trimethylstannyladamantane. An alternative route to organometallic derivatives of triptycene via a Diels—Alder addition reaction of benzyne to the appropriate anthracene is also described.

Introduction

Recently one of us reported on the reactivity of bridgehead adamantyl derivatives of silicon, germanium, tin and titanium [1]. We have now made a preliminary investigation into the reactivity at the bridgehead position of tin derivatives of triptycene. There have been few reported syntheses of these compounds. Wittig et al. [2,3] have prepared di-9-triptycylmercury, but its reactivity was not studied. More recently Märkl and Mayr [4] have synthesised 9-substituted 10-halogenotriptycenes with silicon and mercury as substituent atoms in their attempt to observe transannular nucleophilic substitution at the bridgehead positions. However, no preparative details were given. In this paper, the syntheses of some triptycyltin compounds are described, together with a semi-quantitative assessment of their reactivity, particularly with respect to their adamantyl analogues.

Results and discussion

9-Trimethylstannyl and 9-triphenylstannyltriptycene were prepared in 43 and 38% yields respectively by the method of Wittig et al. [2,3]. Both were airstable, high melting, white crystalline solids (m.p. 295 and 356°C respectively). Using a Wurtz reaction, it is possible to synthesise tetraadamantyl derivatives of tin [1]. The corresponding reaction for the triptycene series, as expected, did not occur, due, in part, to lack of resonance stabilisation at the triptycyl radical. Steric factors are also important (vide infra) which probably account for the failure to synthesise the tetratriptycyl tin derivative from 9-triptycyllithium and $SnCl_4$ (4 : 1 mole ratio), three chlorines only being substituted. There appears to be significant restriction of rotation in 9-alkyl substituents, the rotational barrier being as high as 20—30 kcal. for t-alkyl derivatives [5]. This behaviour is apparent even in methyltriptycenes [6]. Molecular models indicate that the methyl and peri hydrogens are less than 2 Å apart in the most unfavourable conformation whereas in 1-methyladamantane the corresponding conformation has the methyl and C(2) hydrogens 2.5—2.6 Å apart. This predicts that steric effects will be very much more important for triptycyl derivatives than their adamantyl counterparts.

We were unable to prepare 9-trimethylsilyltriptycene by the Wittig route, the main reaction product being triptycene, formed by proton abstraction from either solvent (Et_2O) or trimethylchlorosilane. Similar difficulties were encountered by Taylor [7] in attempts to synthesise tritiated and trimethylsilylated aromatics. Märkl and Mayr [4] apparently experienced no difficulty in preparing the 9-trimethylsilyl-10-halogenotriptycenes from the appropriate lithiated triptycene. It is possible that intra-molecular metal/halogen exchange competes favourably with the corresponding inter-molecular process thus reducing unwanted coupling products. However, no yields were quoted by the authors and protolysis of the lithiated triptycene may still be an important side reaction. An alternative procedure involving Diels—Alder addition of benzyne to 9-trimethylsilylanthracene was tried. Unfortunately, the latter compound proved unexpectedly difficult to make. Very recently Eaborn et al. [8] have reported its synthesis on a small scale using very pure 9-bromoanthracene. The compound is very susceptible to acid cleavage. Evidence for trimethylchlorosilane acting as a proton source comes from its reaction with 9-trichloroacetoxymercurianthracene [9]. In acetone appreciable yields of anthracene (ca. 40%) were obtained whereas the mercurial was recovered unchanged from acetone in the absence of Me_3SiCl. In benzene, which is extremely unlikely to act as a proton source a 24% yield of anthracene was obtained together with a 70% yield of the expected product 9-chloromercurianthracene.

The acidity of the silane reagent can be reduced by increasing the electron density on silicon. This can be achieved by using a silyllithium reagent. Accordingly dimethylphenylsilyllithium was added to 9-bromotriptycene in solvent THF. An exothermic reaction occurred. After the addition was complete the mixture gave a negative Gilman colour test. However, following hydrolysis and the usual work-up procedure, 80% of the 9-bromotriptycene was recovered. The reasons for this anomalous behaviour are not clear; possibly a charge transfer complex is formed between the two reactants. Further work is needed to resolve the question.

In contrast to the silicon analogues, 9-trialkyl- and triaryl-tin derivatives of anthracene were readily prepared. 9-triphenylstannylanthracene underwent a Diels—Alder addition with benzyne to give a high yield of 9-triphenylstannyltriptycene. This method is a good deal easier than the Wittig route and should provide a useful alternative synthetic approach to other organometallic derivatives of triptycene. This is currently being investigated in these laboratories.

Reactions of trimethyl-9-triptycyltin with various electrophiles at room temperature were monitored by PMR. All the reactions studied proceeded slower than the corresponding reactions of 1-adamantyltrimethyltin by a factor of at least 10^3. Bromine reacted to an extent of 81% in 24 h in solvent $CDCl_3$. (0.1 *M* each reagent). Two new singlets appeared at 2.62 and 1.28 ppm and were assigned to methylbromide and dimethyl-9-triptycyltin bromide respectively. No trimethyltin bromide (0.75 ppm) was observed indicating that no appreciable cleavage of the tin—triptycene bond had occurred. Iodine reacted much slower (50% in 6 days) under similar conditions, the progress of the reaction being marked by the appearance of new signals at 2.13 and 1.39 ppm assigned to methyliodide and dimethyl-9-triptycyltin iodide respectively. Again there was no evidence of tin—triptycene bond fission. No reaction was observed with HCl in $CDCl_3$ (0.2 *M*) after 8 days or with mercuric chloride in 1,2-dichloroethane whereas the adamantane derivative reacted quite readily. Triphenyl-9-triptycyltin showed a similar pattern of reactivity with dominant phenyl—tin bond fission, again the reactions being much slower than normal. Table 1 summarises the data described above.

The inertness of the triptycene—tin bond is readily accounted for in terms of steric and electronic factors. Although the bridgehead carbon atom is formally benzylic, the geometry of the structure is such that the sp^3 lobe overlapping with the substituent orbitals is orthogonal with respect to the molecular orbitals of the benzene nuclei, thus preventing resonance stabilisation of any charges which may develop in the transition state. Restricted rotation is likely to be considerably reduced by the increased bond length of the tin—carbon bond. Nevertheless, the bridgehead carbon is very effectively shielded both by the three benzene nuclei to which it is attached and the trimethyltin group. The corresponding adamantane has a much more accessible bridgehead as models again show. What is surprising is the very low reactivity of the tin—methyl bond. Steric constraints on cleavage of the tin—methyl bond would appear to be not very different from those in the adamantyl series and thus the explanation must be made

TABLE I

REACTIVITY OF 1-ADAMANTYL AND 9-TRIPTYCYLTRIMETHYLTIN WITH VARIOUS REAGENTS AT 20 ± 2°C (0.1 *M* IN EACH REACTANT).

Compound[a]	Reagent	Solvent	% reaction[b]	time (h)	% Me—Sn Fission
Me_3SnAd	Br_2	$CDCl_3$	~100	0.5	48
Me_4Sn	Br_2	$CDCl_3$	~100	0.5	100
Ph_3SnAd	Br_2	$CDCl_3$	~100	<0.01	—
Me_3SnTr	Br_2	$CDCl_3$	81	24	100
Me_3SnAd	I_2	$CDCl_3$	~100	<1.0	66
Me_4Sn	I_2	$CDCl_3$	~100	~1.5	100
Me_3SnTr[c]	I_2	$CDCl_3$	50	150	100
Me_3SnAd[c]	HCl	$CDCl_3$	~100	70	89
Me_3SnTr[c]	HCl	$CDCl_3$	0	150	—
Me_3SnAd[c]	$HgCl_2$	acetone-d_6	100	0.5	100
Me_3SnTr[c]	$HgCl_2$	1,2-dichloroethane	0	80	—

[a] Ad = 1-adamantyl, Tr = 9-triptycyl. [b] Determined visually for rapid halogenation reactions. [c] 0.2 *M* in each reactant.

in terms of polar or other effects. The benzene nuclei will exert a $-I$ effect on the bridgehead carbon thus rendering it less susceptible to electrophilic attack. However, it seems unreasonable that such an effect could be transmitted efficiently through three bonds to the methyl carbon atom, unless the central tin atom can in some way facilitate the transmission. Other possible explanations include direct field effects about which little is known in this system, and the formation of π complexes with the aromatic nuclei thus reducing the effective electrophile concentration. Until a detailed kinetic and mechanistic study is made of these reactions, the question must remain unresolved.

Experimental

Solvents diethyl ether, THF, acetone, benzene and dichloromethane were purified by standard methods. Deuteriochloroform was supplied by Ryvan Chemicals Ltd. 9-Bromotriptycene was prepared by the method of Friedman and Logullo [10] with the modification that after removal of the solvent at the end of the reaction cold benzene was added which precipitated most of the product in a crude form which was subsequently purified by column chromatography in the usual manner.

Preparation of 9-trimethylstannyltriptycene and related compounds

(a). Via 9-triptycyllithium. n-Butyllithium (12.2 ml, 1.77 *M*, 21.6 mmol in hexane) was added dropwise to a fine suspension of 9-bromotriptycene (3.6 g, 10.8 mmol) in dry ether (60 ml) with vigorous stirring in an argon atmosphere. The mixture was stirred for 5 h after which it was allowed to stand for 15 min. The supernatant liquid was removed by pipette and trimethyltinchloride (1.8 g, 9.0 mmol) was added together with more dry ether (100 ml). The mixture was stirred for 24 h and allowed to stand for a further 24 h at room temperature. Distilled water (30 ml) was added cautiously followed by benzene (200 ml). The mixture was filtered to remove some insoluble material and the organic phase of the filtrate separated, washed with water and dried over magnesium sulphate to give a white solid (3.4 g). This was recrystallised twice from cyclohexane to give 1.95 g of crystalline product m.p. 294—295°C. (Found: C, 66.4; H, 5.20. $C_{23}H_{22}Sn$ calcd.: C, 66.2; H, 5.28%.) The yield of 9-trimethylstannyltriptycene (nc) was 43%. The NMR spectrum showed an aromatic multiplet at 6.8—8.0 ppm (12H), a methine proton at 5.23 ppm and a methyltin resonance at 0.63 ppm (9H); $J(^{119}Sn-H)$ 52.0, $J(^{117}Sn-H)$ 50.0 Hz. 9-triphenylstannyltriptycene was prepared by the above method except that the product was only slightly soluble in cold benzene. It was filtered from the two phase system used in the extraction process and recrystallised from benzene to give a white crystalline solid m.p. 357°C. (Found: C, 75.5; H, 4.70. $C_{38}H_{28}Sn$ calcd.: C, 75.5; H, 4.82%.) The NMR spectrum showed aromatic multiplets at 6.7—8.2 ppm (27H) and a methine resonance at 5.33 ppm. The yield was 38%. An attempt to prepare tetra-9-triptycyltin by this method yielded tri-9-triptycyltin chloride (30%) m.p. 361°C. (Found: C, 77.7; H, 4.40. $C_{60}H_{39}SnCl$ calcd.: C, 78.8; H, 4.27%.) An attempt to synthesise the compound by a Wurtz reaction failed.

(b). Via Diels—Alder addition. 9-Triphenylstannylanthracene was first prepared by the following method. 9-bromoanthracene (25.6 g, 0.1 mol) was dis-

solved in a minimum volume of dry THF (100 ml) under nitrogen and cooled to —78°C. A solution of n-BuLi (62.4 ml, 1.6 *M* in hexane, 0.1 mol) was added dropwise and after addition the temperature was allowed to rise to 0°C and kept there for 1 h with stirring. A solution of triphenyltinchloride (38.4 g, 0.1 mol) in THF (100 ml) was added dropwise over 2 h. The solvent was removed by rotary evaporation and the residual oil triturated with ethylacetate to induce crystallisation. A white solid (11.6 g) appeared which was recrystallised from benzene to give 9-triphenylstannylanthracene (I) (6.2 g, 12%) m.p. 235—236°C. 5.3 g of I (0.01 mol) was added to isoamyl nitrite (4.7 g, 0.04 mol) in CH_2Cl_2 (100 ml) and treated with anthranilic acid (5.5 g, 0.04 mol) in dry acetone (100 ml). The solution was refluxed for 5 h and allowed to stand overnight whence a precipitate was formed. This was filtered off and the filtrate pumped to dryness to give an oily solid. The combined solids were recrystallised from benzene to give 4.5 g white crystalline solid m.p. 355—357°C whose PMR spectrum was identical with the authentic specimen of 9-triphenylstannyltriptycene prepared above. Yield 75%.

Attempted synthesis of 9-dimethylphenylsilyltriptycene

Tetramethyldiphenylsilane [11] (3 g, 0.011 mol) was treated with finely cut lithium wire (0.42 g, 0.06 g at.) and dry THF (2 ml) under argon [12]. The mixture was stirred vigorously for 0.5 h during which time it acquired a dark brown colour. Dry THF (30 ml) was added dropwise over 1 h and the mixture stirred for a further 3 h. A positive Gilman I [13] test was obtained on the mixture. The mixture was rapidly filtered through a glass wool plug and the filtrate added dropwise to a solution of 9-bromotriptycene (7.4 g, 0.022 mol) in dry THF (50 ml) under argon. The temperature rose 10°C during the addition. A negative Gilman test was obtained 5 min after the addition was complete. The THF was replaced by dry xylene and the mixture refluxed for 16 h, cooled and decomposed with water. After the usual work-up procedure, 5.6 g (80%) 9-bromotriptycene was recovered.

NMR spectra

Spectra were recorded on Varian-A 60A and EM-360 instruments. All chemical shifts reported are in ppm from TMS (δ scale).

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