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STRUCTURE AND DEHYDROGENATION OF SILYLATED DIHYDROANTHRACENES. A NEW ROUTE TO 9- AND 9,10-SILYLATED ANTHRACENES

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Summary

Mono- and di-silylated derivatives of 9,10-dihydro anthracene have been prepared. The *cis* and *trans* isomers of the disilylated compounds were separated and their configurations assigned. Attempted dehydrogenation of the derivatives with sulphur and chloranil led to the formation of anthracene, whereas with n-BuLi/TMED high yields of the corresponding silylated anthracenes were obtained. This affords a new and improved method of synthesis of 9- and 9,10-silylated anthracenes. The mass spectra of the derivatives are also discussed.

Introduction

In attempts to synthesise 9-(trimethylsilyl)anthracene *, trimethylsilyl derivatives of 9,10-dihydroanthracene (9,10-DHA) were prepared in anticipation that they would furnish the desired compound on dehydrogenation. Syntheses of these compounds have been reported [2,3], but no stereochemical assignments were made for the 9,10-bis(trimethylsilyl)-9,10-dihydroanthracene. This paper deals with synthesis and configurational assignment of these compounds, and describes their behaviour under a range of dehydrogenating conditions.

Results and discussion

(i). Structure of 9,10-dihydroanthracenes

The configurations of 9,10-dialkyl-9,10-DHA have been the subject of much controversy in recent years. Alkylation of the anthracene dianion, generated by

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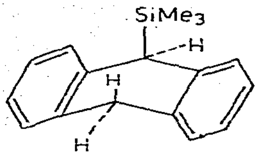
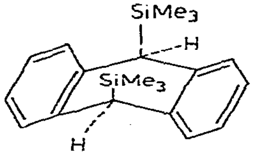
* This compound has now been prepared (vide infra) by Eaborn et al. [1].

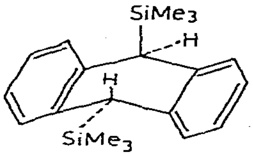
the reaction of alkali metals with anthracene in liquid ammonia and ether solvents, was initially shown to proceed with *cis* stereoselectivity [4], but subsequently diisopropylation was proved to give the trans isomer [5]. Much of the early work in this area was hampered by wrong configurational assignments, and it is only with the recent use of double resonance NMR experiments and the evaluation of Nuclear Overhauser Enhancements (NOE), that the configuration of these molecules has been unambiguously determined. A recent publication by Harvey, Rabideau et al. [6] has summarised the present state of the subject in some considerable detail. The mono- (I) and the di-silylated anthracenes



(I)



(*cis* – II)



(*trans*–II)

(*cis*-II and *trans*-II), were prepared by reductive silylation of anthracene using either n-BuLi, or alkali metals in solvents ether, THF or methylcyclohexane. For complete disilylation, it was found necessary to use a mole ratio of Me_3SiCl to anthracene of at least 4 : 1. It has been shown by numerous workers that reductive alkylation is the major reaction of anthracene under a wide range of metallation conditions. A recent claim that anthracene is polysilylated under similar conditions [7] is at variance with current views and also with the synthetic work presented here. It must be pointed out that no polysilylated derivatives were isolated in the above work and that their characterisation rested heavily on the mass spectra of crude reaction mixtures. In view of the marked tendency of dihydroanthracenes to undergo dehydrogenation under conditions obtaining in the mass spectrometer and with suitable reagents such as sulphur or chloranil (vide infra), the above findings must be treated with some caution.

It is now generally agreed that dihydroanthracenes possess a shallow boat structure [8], the dihedral angle between the benzene ring planes being governed by steric effects associated with the 9- or 10-substituents. There is much evidence to suggest that bulky alkyl groups show a strong preference for a quasi-axial position in such a conformation. In the case of the di-t-butyl-9,10-DHA, the *cis* isomer gave an 8% NOE effect on the H(9), H(10) protons by irradiation of the aromatic protons, whereas the *trans* isomer showed only a 2% enhancement. The corresponding enhancements in H(9), H(10) for irradiation of the t-butyl protons were 10 and 14% respectively [6]. This suggests some flattening of the boat structure of the *trans* isomer. If this is true, then the t-butyl protons will be less shielded than in the pseudo-axial conformation of a true boat. The data in Table 1 lends support to this thesis, although the chemical shift difference between the two isomers is small. However, if the *trans* structure were more planar than the *cis*, the *meso* protons would have more axial character than in the *cis* where they would be pseudo-equatorial. Since it has been shown that pseudo-equatorial protons are more shielded than their axial counterparts [9, 10], the *cis,meso* protons should absorb at a higher field which is contrary to the observed chemical shifts, which makes the above postulate difficult to rationalise.

The double resonance techniques described above have enabled an unambiguous assignment of configuration of the di-t-butyl isomers to be made. The *trans* isomer has the higher melting point and the most shielded *meso* protons, and is the dominant product of the alkylation of 9-t-butyl-9,10-DHA. The t-butyl protons are more shielded in the *cis* isomer, probably due to the strong steric interactions between the t-butyl groups and the *peri* hydrogens which force the molecule to adopt a more boat-like conformation with the t-butyl groups in the pseudo-axial positions. Reductive silylation using an excess of Me_3SiCl gives as the major product a compound melting at 70°C together with a small yield of an isomer melting at 172°C. The chemical shift of the *meso* protons was lower for the latter, which, by analogy with the t-butyl analogue, was assigned the *trans* configuration. The Me_3Si protons were more shielded in the *trans* isomer than the *cis* (Table 1). This can be explained in terms of very strong transannular steric repulsions between the Me_3Si groups, forcing the molecule to adopt a planar, or even an inverted boat conformation, where the silicon atoms are pseudo-equatorial. From inspection of models it is apparent that, compared with the t-butyl analogues, the *peri—meso* interactions are much less important and transannular effects become dominant. Thus the *trans* isomer can exist in a boat-form which is capable of inversion whereas the *cis* isomer has far less mobility. The Me_3Si group in the *trans* isomer can therefore adopt a pseudo-axial position and, as such, is more shielded by the neighbouring aromatic nucleus than the "flatter" *cis* isomer. The melting points of the two isomers also seem to support this assignment, although a final decision must await further, more detailed NMR experiments. If the above assignment is correct, then the major product of reductive silylation is the *cis* isomer, which contrasts strongly with the results obtained for the corresponding alkylations using bulky groups. However, the greater bond length of the Si—C bond compared with the C—C bond will engender a lower order of steric effects which could account for the observed stereochemical course of the reaction.

The pseudo-axial and pseudo-equatorial C(10) protons in 9-t-butyl-9,10-DHA have markedly different chemical shifts [9] (δ 4.17 and 3.70 ppm respectively with J_{gem} 19 Hz) confirming the boat-like nature of the central ring. The trimethylsilyl analogue (I) shows no such differences. The H(9) proton absorbs at 3.43 ppm and appears as a sharp singlet, whilst the H(10) protons appear as a broad signal at 3.78 ppm. Closer inspection of the latter revealed the presence of two singlets separated by $\approx$2 Hz. This indicates that differences due to axial or equatorial stereochemistries have largely disappeared and that the central ring is sensibly planar.

(ii). Dehydrogenation experiments

Attempted dehydrogenations of the trimethylsilylated-9,10-DHA using sulphur or chloranil resulted in the formation of large amounts of anthracene (cf. t-butyl analogues) [11] *. The reactions are undoubtedly free radical in nature and clearly the expulsion of Me_3Si is a more favourable process than removal of a hydrogen atom. For the II isomers, the *cis* form appeared to react

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* The formation of anthracene on treatment of 9-trimethylsilyl-9,10-DHA with sulphur has been reported previously [16].

TABLE 1

NMR SPECTRAL DATA FOR SOME 9,10-DIALKYL-9,10-DIHYDROANTHRACENES[a] AND MONO- AND BIS-TRIMETHYLSILYLATED ANALOGUES (δ (ppm) in CCl_4)

Compound			M.p. (°C)	Aromatic[b]	$-CH_3$	$-CH_2CH_3$	$-CH(CH_3)_2$	$-C(CH_3)_3$	$-Si(CH_3)_3$	H(9)	H(10)
R(9)	R(10)	Isomer									
t-Bu	Me	*cis*	125	6.90—7.37(m)	1.77(d)			0.91(s)		3.73(s)	4.08(q)
t-Bu	Me	*trans*	116	7.00—7.50(m)	1.75(d)			0.93(s)		3.67(s)	4.06(q)
t-Bu	Et	*cis*	56	6.93—7.35(m)		1.29(t)		0.91(s)		3.77(s)	3.77(t)
t-Bu	Et	*trans*	121	7.02—7.58(m)		0.67(t)		0.82(s)		3.66(s)	4.17(t)
t-Bu	i-Pr	*cis*	115	7.08(s)			1.10(d)	1.0(s)		3.88(s)	3.37(d)
t-Bu	i-Pr	*trans*	oil	7.01—7.62(m)			1.25(d)	0.89(s)		3.63(s)	4.08(s)
t-Bu	t-Bu	*cis*	139	6.95—7.35(m)				1.10(s)		4.05(s)	4.05(s)
t-Bu	t-Bu	*trans*	176	6.92—7.42(m)				1.14(s)		3.85(s)	3.85(s)
Me_3Si	H		113	6.89(s)					−0.09(s)	3.43(s)	3.78(s)
Me_3Si	Me_3Si	*cis*	70	6.82(s)					−0.03(s)	3.72(s)	3.72(s)
Me_3Si	Me_3Si	*trans*	172	6.75(s)					−0.18(s)	3.53(s)	3.53(s)

[a] Data from ref. 6. [b] Multiplicity in parentheses (s, singlet; d, doublet etc.).

TABLE 2

MAJOR FRAGMENTATION PATTERN [a] FOR I

Reaction	Fragment lost	Mass change	Metastable
$C_{14}H_{11}SiMe_3^{+\cdot} \rightarrow C_{14}H_{10}SiMe_3^+$	$H^{\cdot}$	252→251	250 [b]
$C_{14}H_{11}SiMe_3^{+\cdot} \rightarrow C_{14}H_{11}SiMe_2^+$	$Me^{\cdot}$	252→237	222.9 [b]
$C_{14}H_{10}SiMe_3^+ \rightarrow C_{14}H_{10}^{+\cdot}$	$Me_3Si^{\cdot}$	251→178	125.7
$C_{14}H_{10}SiMe_3^+ \rightarrow Me_3Si^+$	$C_{14}H_{10}^{\cdot}$	251→73	21.20 [c]
$C_{14}H_{11}SiMe_2^+ \rightarrow Me_2SiH^+$	$C_{14}H_{10}^{\cdot}$	237→59	14.68
$Me_3Si^+ \rightarrow MeSiH_2^+$	C_2H_4	73→45	27.73

[a] Excluding fragmentations of $C_{14}H_{10}^{+\cdot}$ ion. [b] Metastable not observed. [c] Metastable not observed, assignment made by analogy with fragmentation of *cis*-II and *trans*-II.

more readily than the *trans* form, which is in keeping with previous findings in the catalytic dehydrogenation of the corresponding dialkyl derivatives [12].

In contrast to the radical processes, hydrogen is removed selectively from the 9,10 positions by the n-BuLi/TMED complex. Deprotonation occurs very readily to give high yields of the corresponding 9,10-substituted anthracenes and affords a new and improved route to these hitherto rather intractable derivatives. 9-(trimethylsilyl)anthracene and 9,10-bis(trimethylsilyl)anthracene were thus prepared, the former was recently synthesised, after much difficulty, from 9-bromoanthracene [1].

(iii). Mass spectra

The spectra of I, *cis*-II and *trans*-II had several common features. All show parent ions and intense peaks at *m/e* 178 (anthracene ion) and 73 (Me_3Si^+). For I, the spectrum, apart from the peaks due to the Me_3Si group, was remarkably similar to that of anthracene. The major fragmentations appear in Table 2. Loss of a hydrogen atom from the parent ion constituted an important fragmentation since the anthracene ion is formed by loss of a Me_3Si radical from *m/e* 251. In contrast, *cis*-II and *trans*-II (Table 3) do not lose hydrogen but fragment either by loss of Me_3Si radicals, anthracene radicals or Me_4Si. The latter is interesting since presumably the fourth methyl group is abstracted from the transannular Me_3Si group. It was found that the relative abundance of the product ion in this process (*m/e* 236) was higher for the *cis* isomer than for the *trans* (Table 4)

TABLE 3

MAJOR FRAGMENTATION PATTERN [a] FOR *cis*-II AND *trans*-II

Reaction	Fragment lost	Mass change	Metastable
$C_{14}H_{10}(SiMe_3)_2^{+\cdot} \rightarrow C_{14}H_{10}SiMe_3^+$	$Me_3Si^{\cdot}$	324→251	194.4
$C_{14}H_{10}(SiMe_3)_2^{+\cdot} \rightarrow C_{14}H_{10}SiMe_2^+$	Me_4Si	324→236	171.9
$C_{14}H_{10}SiMe_3^+ \rightarrow C_{14}H_{10}^+$	$Me_3Si^{\cdot}$	251→178	126.2 [b]
$C_{14}H_{10}SiMe_3^+ \rightarrow Me_3Si^+$	$C_{14}H_{10}^{\cdot}$	251→73	21.2
$C_{14}H_{10}SiMe_2^+ \rightarrow Me_2SiH^+$	$C_{14}H_{10}^{\cdot}$	236→59	14.7 [b]
$Me_3Si^+ \rightarrow MeSiH_2$	C_2H_4	73→45	27.73

[a] Excluding fragmentations of $C_{14}H_{10}^+$ ion. [b] Metastable not observed, assignment made by analogy with fragmentation of I.

TABLE 4

RELATIVE ABUNDANCE (RA) OF IONS IN THE SPECTRA OF *cis*-II AND *trans*-II

m/e	324	251	236	178	73
RA; *cis*	9.1	18.6	15.5	64.0	100
RA; *trans*	19.4	21.0	4.9	19.2	100

which is in keeping with the configurational assignments made above. Also of interest is the relative abundance of the anthracene ion which is much higher for the *cis* isomer and again is in accord with previous results from catalytic dehydrogenation [12].

The mass spectra of the corresponding anthracenes were interesting in that the 9,10-bis(trimethylsilyl) derivative gave an almost identical spectrum at *m/e* 250 and below, both in terms of peaks and relative intensities, to that of the 9-trimethylsilyl derivative. This indicates that both molecules fragment via a common precursor, presumably the 9-(trimethylsilyl)anthracene ion, though as yet it is not clear how this ion arises from the disubstituted compound. It is possible that a hydrogen is transferred from the Me_3Si group via a cyclic process with elimination of the Me_2SiCH_2 radical, but no metastable ion for this fragmentation (322→250) was observed.

Experimental

The solvents diethyl ether, benzene, tetrahydrofuran, and methylcyclohexane were dried and purified by standard methods. Trimethylchlorosilane and triethylamine were fractionated before use. Blue fluorescent anthracene was obtained by azeotropic distillation with ethyleneglycol.

Preparation of 9,10-bis(trimethylsilyl)-9,10-DHA (cis-II) [2]

Pure anthracene (25 g, 0.14 mol) was mixed with dry benzene (100 ml) and dry Et_2O (100 ml) under an argon atmosphere. 16.7 g of a 30% lithium dispersion (0.72 g-atom) was washed with benzene to remove the petrolatum and then filtered onto a glass wool plug under argon. The plug was immediately transferred to the reaction vessel and the glasswool removed with tweezers. The dark red mixture was stirred for 36 h, then Me_3SiCl (50 ml, 42.8 g, 0.394 mol) added dropwise and the whole stirred for a further 36 h. The mixture was filtered and the filtrate pumped down to yield a pale amber oil (24 g), which partially crystallised on standing overnight at 0°C. The waxy solid was boiled with methanol, filtered and water added until turbidity was observed. The solution was left at 0°C for 1.5 h whence crystallisation occurred to give a white solid (12.9 g), m.p. 70°C. The NMR spectrum showed sharp singlets at δ 0.03 (18 H), 3.72 (2 H) and 6.81 ppm (8 H). The yield of 9,10-bis(trimethylsilyl)-DHA (II) was 28%. (*cis* isomer, see Discussion).

Preparation of 9-trimethylsilyl-9,10-DHA (I) and 9,10-bis(trimethylsilyl)-9,10-DHA (trans-II) [3]

A mixture of anthracene (34.2 g, 0.192 mol) and sodium (9.2 g, 0.40 g-atom) in dry THF (350 ml) was stirred under nitrogen for 2 h to form the deep blue anthracenide. Me_3SiCl (41.7 g, 0.384 mol) in THF (50 ml) was added dropwise over 2.5 h. The resultant green mixture was stirred at room temperature overnight then petroleum ether (60—70°) added and the whole filtered. The filtrate was washed with water (4 × 500 ml) and dried over $MgSO_4$. After filtration the solvent was removed by rotary evaporation to give a golden oil (52.5 g). The oil was triturated with ethanol and gave a white precipitate containing unreacted anthracene. The precipitate was filtered and fractionally crystallised from petroleum ether (60—70°) to give anthracene (1.0 g) and II (1.5 g), m.p. 172°C.

The NMR spectrum showed sharp singlets at δ —0.18 (18 H), 3.53 (2 H), and 6.75 ppm (8 H). The product was assigned as *trans* (see Discussion). Yield 2.5%. The ethanolic filtrate was pumped down to give a golden oil which crystallised at 0°C. The solid was recrystallised from petroleum ether (40—60°) to give 9-(trimethylsilyl)-9,10-DHA (I) (10.3 g), m.p. 110°C. The NMR spectrum of I comprised singlets at δ —0.09 (9 H), 3.43 (1 H), and 6.89 ppm (8 H) and a rather broad doublet at 3.78 ppm (2 H). The filtrate from the petroleum ether recrystallisation was pumped down to give an amber oil (26 g) whose NMR spectrum showed the presence of I (45%), *cis*-II (55%) and a small quantity of *trans*-II (1%). Thus the overall yield of products was I 45%, *cis*-II 23% and *trans*-II 3%. Similarly reactions of anthracene and Me_3SiCl (1 : 2) with (*a*) n-BuLi/Et_3N and (*b*) lithium *N,N,N′,N′*-tetramethylethylenediamine in the solvent methylcyclohexane gave *cis*-II in yields of 21 and 15% respectively. The reaction of 9-bromoanthracene and Me_3SiCl (1 : 2) with lithium in Et_2O gave 6% I and 11% *cis*-II.

Dehydrogenation experiments

(a). With sulphur [13]. I (2.0 g, 7.9 mmol) and powdered sulphur (0.254 g, 7.9 mg-atom) were mixed in a test tube, placed in an Abderhalden apparatus and heated to 190°C (refluxing decalin). Samples were withdrawn at various times and quenched in CCl_4. After filtration, NMR spectra were run. Gradually peaks due to anthracene appeared (singlet at τ 8.12 ppm and two quartets centred at τ 7.50 ppm. After 16 h 34% anthracene was formed and only one peak due to I was observed in the Me_3Si region indicating that dehydrogenation had proceeded with loss of Me_3Si groups. Reactions with mixtures of *cis*-II and *trans*-II show that both Me_3Si groups are eliminated in the form of $(Me_3Si)_2S$ and that the *cis* isomer reacts rather more readily.

(b). With chloranil [14]. I (2.5 g, 0.01 mol) and chloranil (2.5 g, 0.01 mol) were dissolved in *p*-xylene (50 ml) and refluxed for 18 h during which time the mixture became progressively lighter in colour. On cooling, white crystals appeared which were filtered off washed with a little petroleum ether (40—60°) and dried (1.5 g). The NMR spectrum showed anthracene present. A Beilstein test showed the presence of chlorine and the product was probably a mixture or possibly a complex of anthracene and chloranil. The solvent was removed from the filtrate to give 1.8 g of grey solid, the NMR of which showed there to be 73% anthracene and 27% unreacted I. The overall yield of anthracene was >74%.

Using *cis*-II a 90% yield of anthracene was obtained, the contaminating tetrachlorohydroquinone being removed by washing with 5% KOH.

(c). With n-BuLi/N,N,N',N'-tetramethylethylenediamine (TMED) [15]. I (1.0 g, 3.97 mmol) was dissolved in cyclohexane (24 ml) and TMED (12 ml) n-BuLi (10 ml, 1.6 *M* in hexane, 16 mmol) was added rapidly with stirring under an atmosphere of argon. The red colour of the monoanion developed immediately and on bringing the solution to reflux the dianion was formed as indicated by colour change to deep purple. The mixture was refluxed for 1 h, cooled 5 min and cadmium chloride (1.83 g, 10 mmol) added. After ½ h further stirring the colour was discharged and a black precipitate formed. Water (20 ml) was added dropwise and the organic layer separated, washed with 4 × 100 ml portions of water and dried over $MgSO_4$. The solvent was removed by rotary evaporation to give an oil (0.79 g) whose NMR spectrum corresponded to that of 9-(trimethylsilyl)anthracene (80%). The oil crystallised on standing overnight to give pale yellow crystals m.p. 50°C, whose NMR spectrum CCl_4 showed a sharp singlet at δ 0.66 ppm and aromatic multiplets centred at 7.36 (4 H), 7.86 (2 H) and 8.34 ppm (3 H). *

The above experiment was repeated using *cis*-II (3.97 mmol). The oil obtained after rotary evaporation (0.75 g) consisted of 23% unreacted starting material. This was removed by chromatography on alumina with petroleum ether (30—40°) as eluent and using a small UV lamp to monitor the progress of the blue fluorescent anthracene band. A strongly fluorescent white solid was isolated which was recrystallised from MeOH to give colourless needles (0.25 g, m.p. 114.5°C). Solutions of the crystals were very strongly fluorescent. The NMR spectrum of of the product in CCl_4 corresponded to that expected for 9,10-bis(trimethylsilyl)-9,10-DHA (nc) showing a sharp singlet at δ 0.66 ppm (18 H) and two quartets centred at δ 7.34 and 8.30 ppm (8 H). Crude yield 45%. (Found: C, 74.8; H, 8.2. $C_{20}H_{26}Si_2$ calcd.: C, 74.5; H, 8.1%.)

NMR and mass spectra

PMR spectra were run on Varian A60A and EM-360 instruments and chemical shifts are reported in ppm (δ scale) from TMS. Mass spectra were recorded on an AEI MS 12 instrument.

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References

1 C. Eaborn, R. Eidenschink and D.R.M. Walton, J. Organometal. Chem., 96 (1975) 183.
2 A.D. Petrov and T.I. Chernysheva, Dokl. Akad. Nauk SSSR, 84 (1952) 515.
3 M. Maienthal, M. Hellmann, C.P. Haber, L.A. Hymo, S. Carpenter and A.J. Carr, J. Amer. Chem. Soc., 76 (1954) 6392.

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* The δ-values for the aromatic multiplets in ref. 1 are displaced by one unit, presumably as a result of a reporting error.

4 D.F. Lindow, C.N. Cortez and R.G. Harvey, J. Amer. Chem. Soc., 94 (1972) 5406.

5 H.E. Zieger, D.J. Schaeffer and R.M. Padronnagio, Tetrahedron Lett., (1969) 5027.

6 P.P. Fu, R.G. Harvey, J.W. Paschal and P.W. Rabideau, J. Amer. Chem. Soc., 97 (1975) 1145.

7 A.F. Halasa, J. Organometal. Chem., 31 (1971) 369.

8 A.W. Brinkmann, M. Gordon, R.G. Harvey, P.W. Rabideau, J.B. Stothers and A.L. Ternay, Jr., J. Amer. Chem. Soc., 92 (1970) 5912.

9 R. Lapouyade and P. Labandibar, Tetrahedron Lett., 19 (1970) 1589.

10 H.E. Zieger and L.T. Gelbaum, J. Org. Chem., 37 (1972) 1012.

11 W. Carruthers and G.E. Hall, J. Chem. Soc. B, (1966) 861.

12 R.G. Harvey, L. Arzadon, J. Grant and K. Urberg, J. Amer. Chem. Soc., 91 (1969) 4535.

13 P.A. Plattner and E.C. Armstrong, Newer Methods of Preparative Organic Chemistry, Interscience, p. 21, 1948.

14 E. Wolthuis, J. Org. Chem., 26 (1961) 2215.

15 R.G. Harvey and H. Cho, J. Amer. Chem. Soc., 96 (1974) 2434.

16 J.A. Sperry, Univ. of Leicester, Ph.D. Thesis 1960, cited by C. Eaborn and R.W. Bott, in A.G. MacDiarmid (Ed.), Organometallic Derivatives of The Group IV Elements, Vol. 1, Part 1, Dekker, New York, 1968, p. 397.