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INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS

IX*. ANTIMONY–CARBON BOND CLEAVAGE IN TRIALKYLSTIBINES BY SODIUM IN LIQUID AMMONIA. SYNTHETIC APPLICATIONS OF DIALKYL- AND DIPHENYLSTIBYLSODIUM

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SUMMARY

Dialkylstibylsodium compounds have been prepared by cleavage of trialkylstibines with sodium in liquid ammonia. Reactions of the latter with epoxides, *N*-benzoylethylenimine and β-propiolactone have afforded several new functionally substituted organostibines. The different reactivities towards such cleavage of different alkyl groups bound to antimony opens a route to the synthesis of asymmetrically substituted organostibines. Tetraalkyldistibines, which are readily available from the 2/1 reaction of dialkylstibylsodium compounds with 1,2-dichloroethane, have been found to be suitable starting materials for the synthesis of hitherto inaccessible chlorodialkylstibines and trichlorodialkylantimony compounds.

INTRODUCTION

Although considerable information is available on the chemistry of alkali metal derivatives of organoarsines relatively little is known about the corresponding organostibines (*cf.* ref. 2 and refs. cited therein). Wittenberg and Gilman[3] prepared diphenylstibyllithium for the first time by cleavage of an antimony–carbon bond of triphenylstibine with lithium in THF. Later on, Hewerton and Watson[4] observed that triphenylstibine is cleaved much more rapidly by sodium in liquid ammonia. An analytically pure diphenylstibyllithium–dioxane complex was isolated by Issleib and Hamann[5] via metal–hydrogen exchange of diphenylstibine with phenyllithium in diethylether and subsequent addition of dioxane. The corresponding dialkylstibyllithium derivatives, R_2SbLi, in which R = Et[6], t-Bu[7] and cyclohexyl[8], were prepared in essentially the same way. However, the use of the diorganostibines, R_2SbH, which are not readily available makes this procedure less attractive. Dibutylstibyllithium has been prepared by the metal–halogen exchange reaction of bromodibutylstibine with lithium in THF[9]. Similarly, dimethylstibylsodium was obtained by treatment of bromo- or chlorodimethylstibine with sodium in liquid ammonia[10,11]. However, the halodimethylstibine starting materials are not readily

* For part VIII see ref. 1.

available[12]. In the present paper we report a convenient preparation for dialkylstibylsodium derivatives, which together with the diphenyl analogue, have been used for the synthesis of a variety of new organoantimony compounds*.

RESULTS AND DISCUSSION

Preparation of dialkylstibylsodium compounds

The preparation of diphenylstibylsodium by a phenyl group cleavage from triphenylstibine with sodium in liquid ammonia has been known for a decade[4], but, surprisingly, the corresponding reaction with trialkylstibines has never been studied. We observed that upon addition of a trialkylstibine, R_3Sb (R = Me, Et, n-Pr) to a solution of sodium in liquid ammonia in a 1/2 molar ratio, cleavage of one antimony–carbon bond occurs with formation of a dark-red solution of dialkylstibylsodium. For trimethylstibine the cleavage reaction proceeds very fast, as indicated by the colour change from dark-blue to dark-red within a few minutes. This requires 10–15 min for triethylstibine and 4–5 h for tripropylstibine, whereas for tributylstibine hardly any reaction had taken place even after 8 h. Clearly the rate of antimony–alkyl group cleavage decreases in the order of the stability of the anionic species formed.

Interestingly, dichlorotrialkylantimony compounds have been found to be suitable starting materials for the synthesis of dialkylstibylsodium derivatives. *E.g.*, the reaction in liquid ammonia of dichlorotrimethylantimony with sodium in a 1/4 molar ratio affords dimethylstibylsodium in better than 80% yield:

$$Me_3SbCl_2 + 4Na \xrightarrow{NH_3} Me_2SbNa + MeNa + 2NaCl$$

Preparation of ethylpropylbutylstibine and iodomethylethylpropylbutylantimony

The different reactivity towards cleavage by sodium of different alkyl groups bound to antimony provides a tool for the synthesis of asymmetrically substituted organostibines by selectively splitting off one kind of alkyl group. *E.g.* diethylbutylstibine, prepared by the reaction of diethylstibylsodium with butyl bromide, reacts with sodium in liquid ammonia to give a red solution of ethylbutylstibylsodium, which upon addition of propyl bromide affords the asymmetric trialkylstibine, ethylpropylbutylstibine. Upon treatment of this compound with methyl iodide the asymmetric iodotetraalkylantimony compound, iodomethylethylpropylbutylantimony is obtained.

$$Et_3Sb + 2Na \xrightarrow{NH_3liq} Et_2SbNa + EtNa \xrightarrow{BuBr} Et_2SbBu$$

$$Et_2SbBu + 2Na \xrightarrow{NH_3liq} (Et)BuSbNa + EtNa \xrightarrow{PrBr} (Et)PrSbBu$$

$$(Et)PrSbBu + MeI \longrightarrow (Me)(Et)(Pr)BuSbI$$

Preparation of bis(dialkylstibino)methane derivatives and of tetraalkyldistibines

Recently Matsumura and Okawara reported the synthesis of bis(dimethylstibino)methane[11] and bis(diphenylstibino)methane[13] by the reaction of dimethyl-

* *Note added in proof*: After this paper was submitted, two papers[19,20] by Okawara *et al.* appeared dealing with cleavage of alkylantimony compounds by Na in liquid NH_3.

stibyl- and diphenylstibylsodium with methylene chloride in liquid ammonia. Bis(dialkylstibino)methane derivatives can now be very conveniently prepared from trialkylstibines by the following reaction sequence (R = Me, Et, Pr):

$$R_3Sb + 2Na \rightarrow R_2SbNa + RNa \xrightarrow{NH_4Br} R_2SbNa + RH + NaBr + NH_3$$

$$2R_2SbNa + CH_2Cl_2 \rightarrow (R_2Sb)_2CH_2 + 2NaCl$$

Issleib *et al.* have shown that attempts to carry out the corresponding coupling reactions with ethylene dihalides resulted instead in the formation of tetraorganodistibines, R_2SbSbR_2 (R = Et[6], t-Bu[7], cyclohexyl[8], Ph[5]):

$$2R_2SbLi + XCH_2{-}CH_2X \rightarrow R_2SbSbR_2 + CH_2{=}CH_2 + 2LiX$$

The reaction of dialkylstibylsodium compounds, with 1,2-dichloroethane similarly affords tetraalkyldistibines, R_2SbSbR_2 (R = Me, Et, Pr).

Convenient synthesis of chlorodialkylstibines and trichlorodialkylantimony(V) compounds

The only method so far available for the preparation of monohalodialkylstibines involves the thermal cracking of dihalotrialkylantimony compounds[12]. Although bromodialkylstibines may be obtained[14], this method appears to be less suitable for the preparation of chlorodialkylstibines. Only the preparation of Me_2SbCl, in unspecified yield, has been reported[12]. The thermal stability of R_3SbCl_2 (R = Et, Pr) prevents the synthesis of R_2SbCl (R = Et, Pr) by this procedure[15].

We have observed that tetraalkyldistibines readily react with sulfuryl chloride with the formation of chlorodialkylstibines and trichlorodialkylantimony(V) compounds, respectively. In view of the easy availability of tetraalkyldistibines, R_2SbSbR_2 (R = Me, Et, Pr) (*cf.* previous section) a facile synthesis of R_2SbCl and of R_2SbCl_3 (R = Me, Et, Pr) is now available:

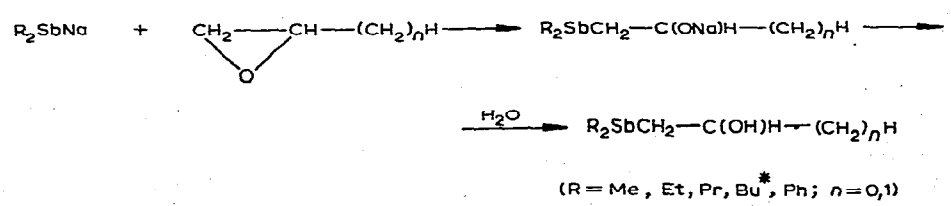
$$2R_2SbNa + ClCH_2CH_2Cl \rightarrow R_2SbSbR_2 + 2NaCl + CH_2{=}CH_2$$

$$R_2SbSbR_2 + SO_2Cl_2 \rightarrow 2R_2SbCl + SO_2$$

$$R_2SbSbR_2 + 3SO_2Cl_2 \rightarrow 2R_2SbCl_3 + 3SO_2$$

Preparation of some functionally substituted organostibines

Like organoplumbyl[16] and organogermyl[17] alkali metal compounds, diorganostibylsodium compounds react rapidly with small-ring heterocycles containing oxygen in the heterocyclic ring. Ethylene oxide and propylene oxide are cleaved instantaneously, to give, after hydrolysis, 2-(diorganostibyl)ethanol and 1-(diorganostibyl)-2-propanol, respectively:



* Bu_2SbNa was prepared by the reaction of Bu_2SbBr with sodium in liquid ammonia.

TABLE 1

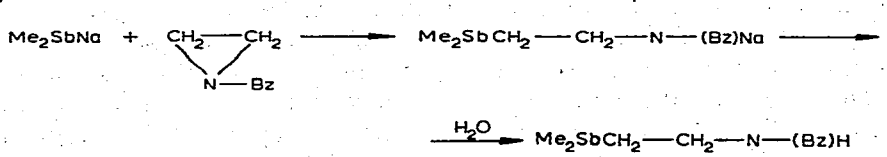
PHYSICAL CONSTANTS, YIELDS, ANALYSES AND PMR DATA OF SOME ORGANOANTIMONY COMPOUNDS PREPARED VIA DIALKYLSTIBYL- AND DIPHENYLSTIBYLSODIUM COMPOUNDS

Compound	*B.p.* (°C/mm)	*Yield* (%)	*Analysis found (calcd.) (%)*		*Chemical shifts*[a,b], *δ (ppm)*[c]
			Sb	*Halogen*	
Et_2SbBu	73–76/9	47	50.66 (51.37)		
(Et)PrSbBu	83–87/8	42	47.79 (48.51)		
(Me)(Et)(Pr)BuSbI	[d]	77	30.81 (30.99)	32.06 (32.30)	
$(Me_2Sb)_2CH_2$	59–61/3[e]	50	75.81 (76.67)		$SbCH_3$ 0.68(s); $SbCH_2Sb$ 0.97(s)
$(Et_2Sb)_2CH_2$	103–105/0.8	68	64.61 (65.16)		$SbCH_2Sb$ 1.02(s)
$(Pr_2Sb)_2CH_2$	115–117/0.2	59	55.85 (56.65)		$SbCH_2Sb$ 0.99(s)
$(Me_2Sb)_2$	53/3.5[f]	79			$SbCH_3$ 0.87(s)
$(Et_2Sb)_2$	82–85/0.6[g]	88	66.95 (66.70)		
$(Pr_2Sb)_2$	92–100/0.01	69	58.45 (58.55)		
Me_2SbCl	78–79/30[h]	60	63.86 (65.01)	17.70 (18.93)	$SbCH_3$ 0.94(s)
Me_2SbCl_3	[i]	100	45.63 (47.16)	40.30 (41.20)	$SbCH_3$ 2.00(s)
Et_2SbCl	83–86/16	75	56.72 (56.55)	16.08 (16.47)	
Et_2SbCl_3	[j]	100	41.97 (42.54)	36.12 (37.16)	$SbCH_2$ 2.93(q); CH_3 1.40(t)
Pr_2SbCl	102–104/7	44	50.07 (50.02)	15.42 (14.56)	
Pr_2SbCl_3	[k]	100	38.44 (38.74)	33.74 (33.84)	$SbCH_2$ 2.85(t); CCH_2C 1.86(m); CH_3 0.73(t)
$Me_2SbCH_2CH_2OH$	97–98/16	85	61.28 (61.93)		$SbCH_3$ 0.77(s); $SbCH_2$ 1.67(t); OCH_2 3.75(t) OH 4.21(u) (in CCl_4)
$Et_2SbCH_2CH_2OH$	75–76/1.5	75	53.87 (54.13)		OCH_2 3.80(t); OH 3.37(u)
$Pr_2SbCH_2CH_2OH$	73–76/0.2	45	48.34 (48.22)		OCH_2 3.76(t); OH 3.76(u) (in CCl_4)
$Bu_2SbCH_2CH_2OH$	100–104/0.4	46	43.28 (43.33)		OCH_2 3.83(t); OH 3.40(u)
$Ph_2Sb(Br_2)CH_2CH_2OH$	[l]	40	25.50 (25.31)	33.61 (33.23)	OCH_2 4.46(t); OH 2.52(u) (in $CDCl_3$)
$Me_2SbCH_2CH(OH)CH_3$	39–41/0.05	81	56.62 (57.71)		$SbCH_3$ 0.69(s); $SbCH_2$ 1.60(d); CCH_3 1.18(d); OCH 3.95(m); OH 2.78(u)

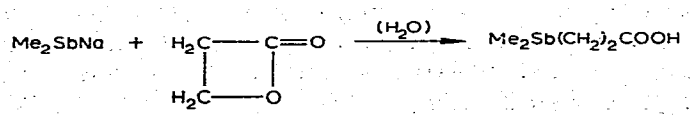
Compound	B.p. (°C/mm)	Yield (%)	Analysis found (calcd.) (%)		Chemical shifts[a,b], δ (ppm)[c]
			Sb	Halogen	
$Et_2SbCH_2CH(OH)CH_3$	63–64/0.3	76	50.64 (50.96)		OCH 4.01(m); OH 2.70(u)
$Pr_2SbCH_2CH(OH)CH_3$	75–76/0.2	57	48.34 (48.22)		OCH 3.82(m); OH 2.53(d)
$Bu_2SbCH_2CH(OH)CH_3$	105/0.4	50	43.28 (43.33)		OCH 3.76(m); OH 2.81(u)
$Ph_2Sb(Br_2)CH_2CH(OH)CH_3$	[m]	30	24.71 (24.60)	32.32 (32.30)	OCH 4.97(m); OH 2.50(u) (in $CDCl_3$)
$Me_2SbCH_2CH_2NH(Bz)$	[n]	66	39.74 (40.58)		$SbCH_3$ 0.68(s); $SbCH_2$ 1.62(t); CH_2N 3.51(m); NH 8.50(t) (in CCl_4)
$Me_2SbCH_2CH_2COOH$	82–86/0.06	48	52.21 (54.12)		$SbCH_3$ 0.56(s); $SbCH_2$ 1.36(t); CH_2 2.34(t); COOH 12.44(s)

[a] In C_6D_6 solution unless indicated otherwise. [b] (Multiplicity) s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; u = unresolved broad signal. [c] Downfield from TMS. [d] M.p. 95–125° (dec.). [e] Ref. 11, b.p. 56–57°/2.5 mm. [f] The compound melts from a red solid to a yellow liquid at 16–17°, *cf.* ref. 10. [g] Ref. 6, a yellow non-distillable liquid. [h] Ref. 12, b.p. 155–160°/750 mm. [i] M.p. 114° (dec.); ref. 12, m.p. 105–110° (dec.). [j] M.p. 70–80° (dec.). [k] M.p. 50–70° (dec.). [l] M.p. 159–163°. Recryst. from cyclohexane. [m] M.p. 148–153°. Recryst. from CCl_4. [n] M.p. 37–42°. Recryst. from pentane.

Like triphenylplumbyllithium[16] and triethylgermylpotassium[17] dimethylstibylsodium failed to react with the nitrogen heterocycle ethylenimine. Acylated ethylenimines react smoothly with triphenylplumbyllithium[16]. Similarly, dimethylstibylsodium reacts with *N*-benzoylethylenimine[18] to give 1-(dimethylstibyl)-2-benzoylaminoethane:



Reaction of dimethylstibylsodium with β-propiolactone proceeds smoothly to give 3-(dimethylstibyl)propionic acid:



Physical constants, yields, analyses and PMR data of the organostibines prepared are listed in Table 1.

EXPERIMENTAL

Reactions involving diorganostibylsodium compounds were performed under dry oxygen-free nitrogen. Liquids were handled by the syringe technique.

PMR spectra were recorded by Miss L. Veldstra and Miss T. Volp, using a Varian Associates T 60 NMR spectrometer. Antimony and halogen analyses were performed by Mrs. J. M. Mak–Oosterlaken.

Ethylpropylbutylstibine and iodomethylethylpropylbutylantimony

Diethylbutylstibine. Triethylstibine (20.9 g, 0.1 mol) was added to a solution of sodium (4.6 g, 0.2 mol) in liquid ammonia (200 ml). Within 15 min the colour of the reaction mixture had changed from dark-blue to red. Stirring was continued for 1 h, then butyl bromide (27.4 g, 0.2 mol) was added dropwise, leading to a decolouration of the reaction mixture. Ammonia was allowed to evaporate, and diethyl ether (100 ml) and water (50 ml) were added to the reaction residue. The diethyl ether layer was separated, dried on Mol. sieve 4A, and subsequently evaporated. The residual liquid was distilled to give 11.2 g of colourless diethylbutylstibine, b.p. 73–76°/9 mm. Yield 47%.

Ethylpropylbutylstibine. Diethylbutylstibine (9.5 g, 0.04 mol) was added to a solution of sodium (1.9 g, 0.08 mol) in liquid ammonia (150 ml). Stirring was continued for 1.5 h, then propyl bromide was added dropwise in excess, causing decolouration of the red reaction mixture. Work-up as described above, followed by distillation, gave 4.2 g of ethylpropylbutylstibine, b.p. 83–87°/8 mm. Yield 42%.

Iodomethylethylpropylbutylantimony. A mixture of ethylpropylbutylstibine (1.9 g, 0.008 mol) and methyl iodide (5 ml) was refluxed for 7 h. Evaporation of the excess of methyl iodide resulted in the isolation of a pale yellow solid which was recrystallized from benzene/pentane to give 2.3 g of iodomethylethylpropylbutylantimony as a pale yellow solid, m.p. 93–125° (dec.). Yield 77%.

Bis(dialkylstibino)methane derivatives

Bis(dimethylstibino)methane. Trimethylstibine (6.7 g, 0.04 mol) was added to a solution of sodium (1.9 g, 0.08 mol) in liquid ammonia (200 ml). Within 10 min the colour of the reaction mixture had changed from dark-blue to dark-red. Stirring was continued for an additional 20 min, then ammonium bromide (4.0 g, 0.04 mol) was added. Dropwise addition of 2.0 g of methylene chloride resulted in instantaneous reaction, leading to decolouration. Ammonia was allowed to evaporate and diethyl ether (80 ml) and water (50 ml) were added to the residue. The diethyl ether layer was separated, dried on Mol. sieve 4A and subsequently evaporated. The residual liquid was distilled to give 3.2 g of pale yellowish bis(dimethylstibino)methane, b.p. 59–61°/3 mm. Yield 50%.

Bis(diethylstibino)methane. Triethylstibine (20.9 g, 0.1 mol) was added to a solution of sodium (4.6 g, 0.2 mol) in liquid ammonia (200 ml). Within 15 min the colour of the reaction mixture had changed from dark-blue to red. Stirring was continued for 1.5 h, then ammonium bromide (9.8 g, 0.1 mol) was added. Dropwise addition of 4.3 g of methylene chloride resulted in instantaneous reaction. Work-up of the reaction mixture afforded 12.7 g of pale yellowish bis(diethylstibino)methane, b.p. 103–105°/0.8 mm. Yield 68%.

Bis(dipropylstibino)methane. Tripropylstibine (12.5 g, 0.05 mol) was added to a solution of sodium (2.3 g, 0.1 mol) in liquid ammonia (200 ml). After stirring for 4 h the colour of the reaction mixture had changed from dark-blue to dark-red. Using the procedure described above, 6.3 g of pale yellowish bis(dipropylstibino)methane, b.p. 115–117°/0.2 mm was obtained. Yield 59%.

Tetraalkyldistibines

(*a*) *From trialkylstibines.* 1,2-Dichloroethane was added dropwise to an ammonia solution of dialkylstibylsodium (0.1 mol) and alkylsodium (0.1 mol) prepared as described above, until decolouration was complete. Work-up of the reaction mixture in the usual way, followed by distillation, afforded tetraalkyldistibines as yellow liquids which are stable towards water, but highly sensitive towards oxidation by air-oxygen. Upon distillation of $Pr_2SbSbPr_2$, partial decomposition, with formation of antimony metal, took place.

(*b*) *Tetramethyldistibine from dichlorotrimethylantimony.* Sodium (5.0 g, 0.22 mol), cut in small pieces, was added to a suspension of dichlorotrimethylantimony (12.0 g, 0.05 mol) in liquid ammonia (200 ml). Instantaneously a reaction took place, and initially a greenish oil precipitated. When 0.1 mole of sodium was consumed a colourless solution was obtained. Further addition of sodium (0.12 mol) resulted in the formation of a dark-red solution of dimethylstibylsodium in liquid ammonia. Reaction with 1,2-dichloroethane (6.0 g, 0.06 mol) in diethyl ether (100 ml) gave a brown reaction mixture, which upon standing became black, due to the deposition of a minor amount of antimony metal. Work-up in the usual way gave 6.0 g of yellow tetramethyldistibine. Yield 79%.

Chlorodialkylstibines and trichlorodialkylantimony compounds

Chlorodimethylstibine. A solution of tetramethyldistibine (2.4 g, 0.008 mol) in methylene chloride (40 ml) was cooled to −78°. Dropwise addition of sulfuryl chloride (1.1 g, 0.008 mol) in methylene chloride (10 ml) resulted in the formation of an orange solution. Evaporation of the solvent and distillation of the residual liquid gave 1.8 g of pale yellow chlorodimethylstibine, b.p. 78–79°/30 mm. Yield 60%.

Chlorodiethylstibine (yellow liquid, b.p. 83–86°/16 mm) and chlorodipropylstibine (yellow liquid, b.p. 102–104°/7 mm) were prepared from tetraethyl- and tetrapropyldistibine by the same reaction procedure.

Trichlorodimethylantimony. A solution of tetramethyldistibine (1.2 g, 0.004 mol) in methylene chloride (40 ml) was cooled to −78°. Dropwise addition of sulfuryl chloride (1.6 g, 0.012 mol) resulted in the precipitation of a colourless solid, which at room temperature dissolved to give a clear solution. Evaporation of the solvent afforded 2.0 g of trichlorodimethylantimony as a colourless solid with m.p. 104–107° (dec.). Yield 100%.

Trichlorodiethylantimony and trichlorodipropylantimony were prepared from tetraethyl- and tetrapropyldistibine by the same procedure.

Functionally substituted organostibines

2-(*Dimethylstibyl*)*ethanol.* Trimethylstibine (12.5 g, 0.075 mol) was added to a solution of sodium (3.5 g, 0.15 mol) in liquid ammonia (100 ml). After stirring for 0.5 h, ethylene oxide gas was bubbled into the dark-red solution. Immediately a reaction took place and the reaction mixture was decolourized. Work-up in the usual way followed by distillation gave 12.6 g of colourless 2-(dimethylstibyl)ethanol, b.p. 97–98°/16 mm. Yield 85%.

In a similar way were prepared 2-(diethylstibyl)ethanol, 2-(dipropylstibyl)-ethanol, 2-(dibutylstibyl)ethanol, 1-(dimethylstibyl)-2-propanol, 1-(diethylstibyl)-2-propanol, 1-(dipropylstibyl)-2-propanol, 1-(dibutylstibyl)-2-propanol, 1-(dimethyl-

stibyl)-2-benzoylaminoethane and 3-(dimethylstibyl)propionic acid. 2-(Diphenylstibyl)ethanol and 1-(diphenylstibyl)-2-propanol which were both obtained as oils, were not isolated as such, but were converted into the corresponding crystalline dibromoorganoantimony(V) derivatives by treatment with one equivalent of bromine in carbon tetrachloride.

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REFERENCES

1 H. A. Meinema and J. G. Noltes, *J. Organometal. Chem.*, 37 (1972) C31.
2 G. O. Doak and L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony and Bismuth*, Wiley-Interscience, New York, 1970, p. 133.
3 D. Wittenberg and H. Gilman, *J. Org. Chem.*, 23 (1958) 1063.
4 W. Hewerton and H. R. Watson, *J. Chem. Soc.*, (1962) 1490.
5 K. Issleib and B. Hamann, *Z. Anorg. Allg. Chem.*, 343 (1966) 196.
6 K. Issleib and B. Hamann, *Z. Anorg. Allg. Chem.*, 339 (1965) 289.
7 K. Issleib, B. Hamann and L. Schmidt, *Z. Anorg. Allg. Chem.*, 339 (1965) 298.
8 K. Issleib and B. Hamann, *Z. Anorg. Allg. Chem.*, 332 (1964) 179.
9 S. Herbstman, *J. Org. Chem.*, 29 (1964) 986.
10 A. Burg and L. R. Grant, *J. Amer. Chem. Soc.*, 81 (1959) 1.
11 Y. Matsumura and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 449.
12 G. T. Morgan and G. R. Davies, *Proc. Roy. Soc. (London), Ser. A*, 110 (1926) 523.
13 Y. Matsumura and R. Okawara, *J. Organometal. Chem.*, 25 (1970) 439.
14 E. A. Besolova, V. A. Foss and I. F. Lutsenko, *Zh. Obshch. Khim.*, 38 (1968) 267.
15 H. A. Meinema, unpublished results.
16 L. C. Willemsens and G. J. M. van der Kerk, *J. Organometal. Chem.*, 4 (1965) 34.
17 E. J. Bulten and J. G. Noltes, *J. Organometal. Chem.*, 29 (1971) 409.
18 A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, (1948) 1919.
19 S. Sato, Y. Matsumura and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 8 (1972) 837.
20 S. Sato, Y. Matsumura and R. Okawara, *J. Organometal. Chem.*, 43 (1972) 333.