

INVESTIGATIONS ON ORGANOGERMANIUM COMPOUNDS XII*. REACTIONS OF TRIALKYLGERMANYL ALKALI METAL COMPOUNDS IN HEXAMETHYLPHOSPHORIC TRIAMIDE (HMPT) WITH SOME INORGANIC AND ORGANIC COMPOUNDS**

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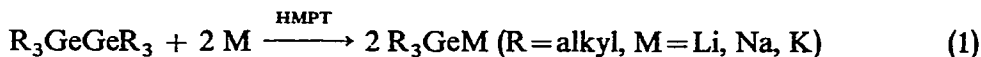
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SUMMARY

Trialkylgermyl alkali metal compounds in HMPT have been found to be highly reactive nucleophiles. Reactions with some inorganic and organic compounds, such as oxygen, carbon dioxide, inorganic and organic halides, aldehydes, ketones, epoxides and lactones are described. Several new carbon-functional organogermanium compounds have been characterized.

INTRODUCTION

In a previous paper¹ we reported a satisfactory method for the preparation of trialkylgermyl alkali metal compounds. This involves the cleavage of hexaalkyldigermanes with alkali metals in hexamethylphosphoric triamide at room temperature:



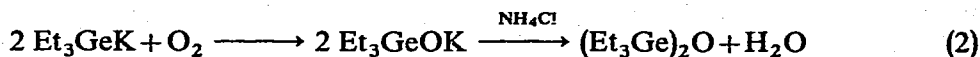
The reactions of trialkylgermyl alkali metal derivatives in HMPT with inorganic and organic compounds described in the present paper, demonstrate the versatility and high reactivity of these reagents.

Reactions with organometallics will be dealt with in a subsequent paper.

RESULTS AND DISCUSSION

Reactions with oxygen and carbon dioxide

Solutions of trialkylgermyl alkali metal compounds in HMPT react rapidly with oxygen at room temperature. Per mole of reagent one half mole of oxygen is consumed. Decomposition of the reaction mixture with ammonium chloride gives quantitatively the corresponding oxides, *viz.*:

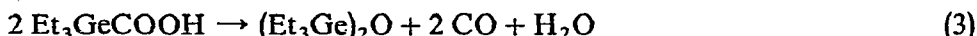


* For Part XI see ref. 1.

** Taken from the Ph.D. thesis of E.J.B., State University of Utrecht, 1969.

Similar results have been reported for triphenylgermylsodium².

Treatment of triethylgermylpotassium with carbon dioxide followed by very careful acidification yielded triethylgermylcarboxylic acid, Et_3GeCOOH , the first representative of a trialkyl group IV metal carboxylic acid³. More recently this method has been applied to the preparation of trimethylgermylcarboxylic acid⁴. On heating, triethylgermylcarboxylic acid decomposes at about 100° according to:



In contrast, thermolysis of triphenylgermylcarboxylic acid⁵ starts only at 190°. Slow decomposition also occurs on treatment with dilute mineral acids, reaction being vigorous with concentrated acids:



No gas evolution was observed with a dilute (4 N) aqueous solution of sodium hydroxide. The latter observations were rather unexpected as triphenylsilylcarboxylic acid has been reported to be stable against acids but highly sensitive towards bases^{5,6}.

Reactions with some inorganic and organic halides

Trialkylgermyl alkali metal compounds react rapidly with inorganic and organic halides (*cf.* Table 1).

TABLE 1

REACTION OF Et_3GeK WITH SOME GROUP IV HALIDES AT -70°a

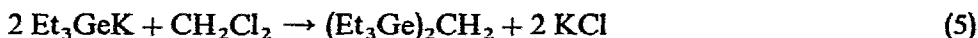
Substrate	Products isolated	
	$\text{Et}_3\text{GeGeEt}_3$ (%)	Other (%)
CCl_4	60	
CBr_4	60	
CHCl_3	70	
CH_2Cl_2	25	$(\text{Et}_3\text{Ge})_2\text{CH}_2$ (65)
CH_3Cl	6 ^b	Et_3GeCH_3 (94) ^b
HSiCl_3	50	
GeCl_4	60	
GeI_2	20	$(\text{Et}_3\text{Ge})_3\text{GeCH}_3$ (42) ^c

^a Addition of the reagent to a solution of the substrate; per chlorine atom one equivalent of reagent is used. ^b Determined by GLC analysis. ^c After treatment with methyl iodide.

Reaction with carbon tetrachloride, carbon tetrabromide, as well as with chloroform only yielded the corresponding digermane, together with some unidentified black resin. In order to determine whether in the reaction of triethylgermyllithium with carbon tetrachloride dichlorocarbene was involved as an intermediate, the reaction was repeated in cyclohexene as the solvent. Again, hexaethyldigermane and carbon black were obtained but no trace of 1,1-dichloronorcarane could be detected (GLC). Germanium tetrachloride and trichlorosilane also failed to give coupling products in HMPT. It was recently reported^{7,8} that in the reaction of trichlorosilane with a solution of Et_3GeLi in THF the coupling product tris(triethylgermyl)silane

is formed. Apparently, the solvent is of decisive importance in this type of reaction (*cf.* ref. 1).

Treatment of Et_3GeK with dichloromethane gave exclusively disubstitution (5), irrespective whether a 1/1 or 2/1 molar ratio of reactants was used. Even with a ten-fold excess of dichloromethane bis(triethylgermyl)methane was the only coupling product formed. Apparently substitution of the second chlorine atom proceeds much faster than substitution of the first one. Similar results have been obtained with triphenylplumbyllithium⁹.

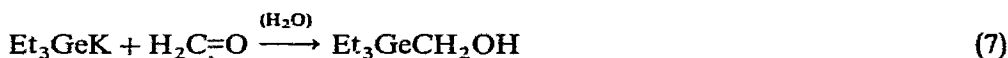


Treatment of Et_3GeLi with GeI_2 followed by methyl iodide gave a moderate yield of tris(triethylgermyl)methylgermane*.

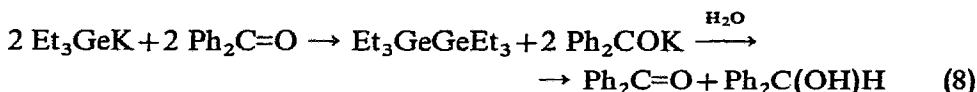


Reactions with compounds containing carbon-oxygen bonds

As was expected trialkylgermyl alkali metal compounds react rapidly with organic materials containing a carbon-oxygen bond, such as aldehydes, ketones and small-ring heterocycles. Among the aldehydes and ketones investigated, only formaldehyde gave the expected adduct, *viz.* (triethylgermyl)methanol:



Reactions with acetaldehyde, acetone and acetophenone gave exclusively triethylgermane. Because of the acidic character of these compounds (*cf.* ref. 1) metalation predominates over addition. Reaction of triethylgermylpotassium with benzophenone in HMPT solution did not give the expected carbinol either. In this case a deep blue solution was formed and, after the usual work-up procedure hexaethylidigermane, benzophenone and diphenylmethanol were obtained. Presumably benzophenone had been reduced to the corresponding ketyl (blue colour), which upon hydrolysis affords equal amounts of benzophenone and diphenylmethanol, according to:



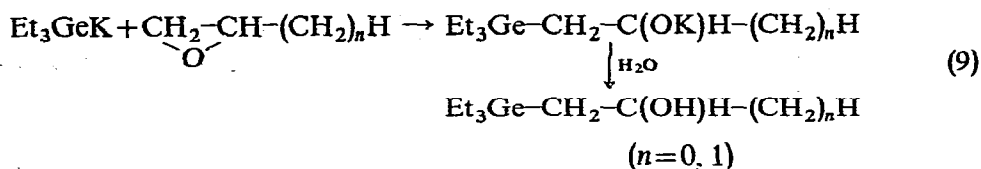
A similar reaction course has been observed with triphenylstannylsodium¹⁰, whereas with triphenylgermyllithium the addition product (triphenylgermyl)diphenylmethanol is formed exclusively¹¹.

As reported recently¹² reaction of Et_3GeLi in THF with benzophenone does give rise to the formation of a moderate amount of (triethylgermyl)diphenylmethanol. This demonstrates once again the strong influence of the solvent used in reactions with germyl alkali metal compounds.

* This experiment was performed by Dr. G. Manuel (University of Toulouse, France) during a short stay at Utrecht.

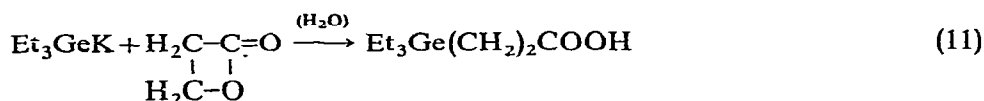
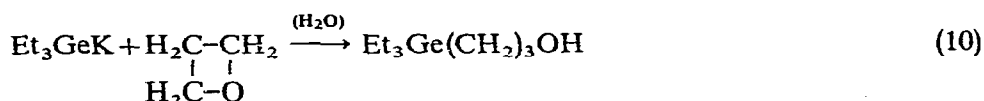
No reaction takes place between Et_3GeK and cyclohexanone in HMPT.

The three-membered ring compounds ethylene oxide and propylene oxide are cleaved instantaneously at room temperature to give 2-(triethylgermyl)ethanol and 1-(triethylgermyl)-2-propanol, respectively:



Just as with triphenylplumbyllithium¹³ the nitrogen-heterocycle ethylenimine failed to react with triethylgermylpotassium.

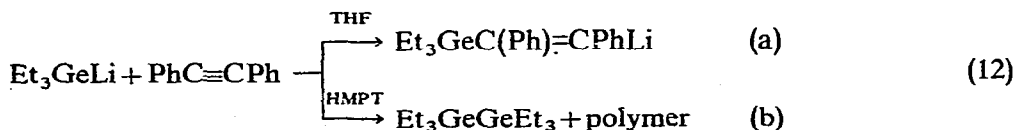
Reaction with the four-membered ring compounds trimethylene oxide and β -propiolactone proceeded smoothly to give 3-(triethylgermyl)-1-propanol and 3-(triethylgermyl)propionic acid respectively:



Cleavage of a five-membered ring of tetrahydrofuran did not occur at room temperature. Because of the low thermal stability of the reagent¹ this reaction could not be studied under more drastic conditions.

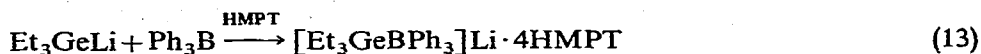
Miscellaneous reactions

As reported recently, reaction of triethylgermyllithium with diphenylacetylene in THF solution gives almost quantitatively the expected adduct eqn. (12a)¹². In contrast, we found that in the strongly basic solvent HMPT hexaethyldigermane is the main product, together with a dark-brown polymeric material containing no germanium (eqn. 12b).



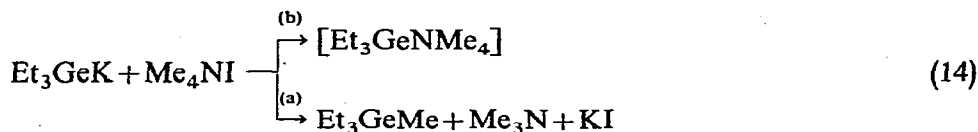
Similar results were obtained on treating triethylgermylpotassium with 2,3-dimethylbutadiene. Triethylgermyllithium fails to react with cyclohexene, in both HMPT and THF¹².

Treatment of triethylgermyllithium with triphenylboron gave a solid which analysed for the ate complex lithium (triethylgermyl)triphenylborate, complexed with four molecules of HMPT.



Similar results were obtained previously with triphenylgermyllithium¹⁴.

Attempts to replace the cation of triethylgermylpotassium by a tetramethylammonium group resulted in the formation of methyltriethylgermane:



It could not be decided whether the methyltriethylgermane had been formed by (a) direct dealkylation of the substrate or (b) via the intermediate formation of (tetramethylammonium)triethylgermane.

Physical constants, yields, analyses and PMR data of the organogermanes prepared are presented in Table 2.

EXPERIMENTAL

All reactions involving trialkylgermyl alkali metal compounds were performed in rigorously dried glass apparatus in an atmosphere of dry, oxygen-free nitrogen. Liquids were handled by the syringe technique. Unless indicated otherwise experiments were performed with 0.6–0.7 *N* solutions of R_3GeM in HMPT, prepared by cleavage of the corresponding R_3GeGeR_3 with alkali metals¹. The NMR spectra were recorded by Miss L. Veldstra and Mr. J. W. Marsman, using a Varian Associates HA-100 NMR spectrometer. GLC analyses, performed by Mrs. G. G. Versluis-de Haan, were made by means of F & M Gas chromatographs models 500 and 810 with katharometer detection, using helium as the carrier gas. The microanalyses of carbon and hydrogen were performed by Mrs. J. van Gool-Uytewaal, Miss H. G. M. Stolwijk and Mr. W. J. Buis at the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

Triethylgermylcarboxylic acid

A solution of triethylgermylpotassium in HMPT (35 ml, containing 31 mmoles of triethylgermylpotassium and 0.10 mmoles of hexaethyldigermene) was treated with an excess of solid carbon dioxide. The colourless reaction mixture obtained was diluted with 60 ml of water, adjusted with 4 *N* hydrochloric acid to pH 8, and extracted twice with 20 ml of diethyl ether to give a few drops of hexaethyldigermene (identified by GLC). The water/HMPT layer was acidified with 0.5 *N* hydrochloric acid to pH 6 and extracted twice with 20 ml of diethyl ether to give 1.9 g of crude triethylgermylcarboxylic acid (n_D^{20} 1.4625). Further acidification of the water/HMPT layer to pH 4 and subsequent extraction gave another, small amount of product (0.3 g, n_D^{20} 1.4630). In the PMR spectrum of the crude product (2.2 g, 34%) the ratio of the integrated intensities ethyl protons/acid proton was found to be 19 to 1 (calcd. 15 to 1); chlorine content: 0%, germanium content: 37.1% (calcd. 35.45%). The crude product was dissolved in 10 ml of 4 *N* sodium hydroxide and extracted twice with 10 ml of light petroleum (40–60°). Thereupon, the water layer was adjusted at pH 4 with 4 *N* hydrochloric acid and extracted twice with 10 ml of light petroleum (40–60°) to give pure triethylgermylcarboxylic acid, n_D^{20} 1.4621. The PMR spectrum showed two signals with the expected 15/1 ratio.

TABLE 2
 PHYSICAL CONSTANTS, YIELDS, ANALYSES AND PMR DATA OF SOME ORGANOGERMANES PREPARED VIA TRIALKYLGERMYL ALKALI METAL COMPOUNDS

Compound	B.p. (°C/mm)	n_D^{20}	Yield ^a (%)	Analysis (%)			Chemical shifts (multiplicity) ^b δ (ppm) ^c		
				Found			Calcd.		
				C	H	O	C	H	O
Et_3GeCOOH		1.4621	34	41.0	8.0	41.05	7.88	COOH 11.7 (s)	
$(\text{Et}_3\text{Ge})_2\text{CH}_2$	138-139/14	1.4822	65	46.9	9.6	46.81	9.67	GeCH_2Ge -0.19 (s)	
$(\text{Et}_3\text{Ge})_3\text{GeCH}_3^d$	144-145/0.02	1.5468	20	40.6	8.3	40.25	8.53	CH_3Ge 0.44 (s)	
$\text{Et}_3\text{GeCH}_2\text{OH}$	86/15	1.4659	32	44.3	9.8	44.06	9.51	OCH_2 3.65 (s); OH 2.92 (u)	
$\text{Et}_3\text{GeCH}_2\text{CH}_2\text{OH}^e$	52-55/0.09	1.4682	80	46.6	9.8	46.90	9.84	OCH_2 3.71 (t ^g); OH 3.92 (u)	
$\text{Et}_3\text{GeCH}_2\text{CH}_2\text{CH}_2\text{OH}^f$	94-98/0.2	1.4689	66	49.5	10.1	49.39	10.14	CCH_2C 1.55 (m); OCH_2 3.46 (t ^g); OH 3.96 (u)	
$\text{Et}_3\text{GeCH}_2\text{C}(\text{OH})\text{HCH}_3^g$	62-63/0.45	1.4686	35	49.8	10.4	49.39	10.14	OCH 3.92 (m); OH 2.68 (u)	
$\text{Et}_3\text{GeCH}_2\text{CH}_2\text{COOH}^h$	122-124/1	1.4679	15	46.6	8.7	46.42	8.66	CCH_2C 2.35 (t ^g); COOH 11.87 (s)	
$\text{Me}_3\text{GeCH}_2\text{CH}_2\text{COOH}^i$	104-106/14	1.4492	25	38.3	7.4	37.77	7.40	GeCH_2 0.14 (s); GeCH_2 0.99 (t ^m); CH_2 2.38 (t ^m); COOH 12.00 (s)	
$[\text{Et}_3\text{GeBPh}_3]\text{Li}\cdot 4\text{HMPT}$	156-159 ⁿ			51.4	9.9	51.22	9.13	CH_2Ge 0.43 (g); CH_3Ge 0.74 (t)	

^a Generally crude product yields of 60-90% were obtained. Repeated fractionation was necessary to remove tenacious traces of solvent. ^b s=singlet; t=triplet; q=quartet; m=multiplet; u=unresolved broad signal. Only under super dry conditions signals due to the -CHOH- unit were split-up by mutual interaction. ^c Downfield from tetramethylsilane. ^d Mol.wt. found 540, calcd. 566.95. ^e Cf. ref. 15. ^f Cf. ref. 16. ^g Cf. ref. 17. ^h Cf. ref. 18. ⁱ Prepared with Me_3GeLi ; J 8.7 Hz. ⁿ J 6.7 Hz. ^m J 8.4 Hz. ^o J 7.9 Hz. ^p m.p.

Bis(triethylgermyl)methane

A solution of triethylgermylpotassium in HMPT (40 ml, 36.0 mmoles of reagent) was added slowly to 37.4 g (440 mmoles) of dichloromethane at -70° . The faintly yellowish reaction mixture was diluted with 100 ml of water and extracted twice with 25 ml of benzene. The combined benzene layers were treated once with 25 ml of concentrated hydrochloric acid. Careful fractionation gave 7.8 g (65%) of bis(triethylgermyl)methane, b.p. $138-139^{\circ}/14$ mm, n_D^{20} 1.4822.

The reactions of triethylgermylpotassium with carbon tetrachloride, carbon tetrabromide, chloroform, germanium tetrachloride and trichlorosilane (Table 1) have been performed in a similar way, albeit with equimolar amounts of reactants. Reaction with methyl chloride has been carried out similarly with 150% excess of this compound. In the latter case the reaction mixture was analysed by GLC.

Tris(triethylgermyl)methylgermane

A solution of 30 mmoles of triethylgermyllithium in HMPT was slowly added to a stirred suspension of 10 mmoles of germanium diiodide in 100 ml of pentane at -70° . The temperature of the partly solid, brown reaction mixture was slowly raised to 20° and the mixture was treated with an excess of methyl iodide. Distillation of the oily liquid obtained by extraction gave 2.0 g (42%) of hexaethyldigermane, b.p. $142-145^{\circ}/20$ mm, n_D^{20} 1.4985 and 1.1 g (20%) of tris(triethylgermyl)methylgermane, b.p. $144-145^{\circ}/0.02$ mm, n_D^{20} 1.5468, d_4^{20} 1.281. UV: λ_{\max} 258 nm, ϵ 39.500.

(Triethylgermyl)methanol

By means of a slow stream of nitrogen gaseous formaldehyde—prepared by thermal depolymerization of paraformaldehyde at $150-160^{\circ}$ —was passed over the surface of a vigorously agitated solution of 25 mmoles of triethylgermylpotassium in HMPT. To the colourless reaction mixture obtained were added 5 ml of 4 N hydrochloric acid and subsequently 40 ml of water. Finally, the reaction mixture was neutralized (pH 7) with 4 N hydrochloric acid and extracted four times with 20 ml of pentane. The combined pentane layers were treated four times with 20 ml of water and dried. Distillation of the crude product (4.8 g) obtained, gave 1.5 g (32%) of (triethylgermyl)methanol, b.p. $86^{\circ}/15$ mm, n_D^{20} 1.4659.

Reaction of triethylgermylpotassium with acetone

A solution of triethylgermylpotassium (1 ml, 0.66 mmole) in HMPT was added to 800 μ l (\approx 12 mmoles) of redistilled acetone (dried on molecular sieves). The resulting colourless solution was treated with 75 μ l (1 mmole) of ethyl iodide and analysed by GLC. In this way it was established that 0.64 mmole (97%) of triethylgermane had been formed. No trace of tetraethylgermane was observed. In addition to acetone some diacetone alcohol was also detected.

Similar results were obtained with acetaldehyde and acetophenone. With cyclohexanone no reaction was observed.

Reaction of triethylgermylpotassium with benzophenone

A solution of triethylgermylpotassium (30.0 mmoles) in HMPT was added to a solution of benzophenone (5.5 g, 30.0 mmoles) in 20 ml of HMPT to give a deep blue solution. The mixture was decomposed (decolouration) with 4 N hydrochloric acid,

diluted with 70 ml of water and adjusted to pH 7. Extraction with pentane and cooling of the pentane solution to 0° gave 1.44 g of a crystalline product, m.p. 62–64°. The PMR spectrum as well as IR spectrum of this product were identical with that of diphenylmethanol (8 mmoles). Evaporation of the pentane filtrate at 50° *in vacuo* yielded a liquid residue consisting of two layers. The entire residue was distilled to give 4.1 g of a liquid that appeared to be (GLC) impure hexaethyldigermane (~12 mmoles, 80%) and 2.3 g of a liquid that consisted of benzophenone (~12 mmoles), contaminated with some hexaethyldigermane and some diphenylmethanol.

2-(Triethylgermyl)ethanol

Ethylene oxide (1.10 g, 25.0 mmoles) was added slowly to a solution of 27.0 mmoles of triethylgermylpotassium in HMPT. The entire experiment was performed at 1° in view of the low boiling point of ethylene oxide (13°). The yellow reaction mixture was decomposed with 7 ml of water, adjusted to pH 7 with dilute hydrochloric acid and extracted with pentane. Distillation gave 4.1 g (80%, based on ethylene oxide) of 2-(triethylgermyl)ethanol, b.p. 52–55°/0.09 mm, n_D^{20} 1.4682.

In a similar way were prepared 1-(triethylgermyl)-2-propanol (35%), 3-(triethylgermyl)-1-propanol (66%), 3-(triethylgermyl)propionic acid (15%) and 3-(trimethylgermyl) propionic acid (25%). In the case of the last two compounds purification was performed as described for triethylgermylcarboxylic acid.

Lithium (triethylgermyl)triphenylborate

A solution of triethylgermyllithium (17.0 mmoles) in HMPT (24 ml) was added slowly to a solution of 4.8 g (19.8 mmoles) of triphenylboron in 50 ml of THF. Evaporation of the THF *in vacuo* gave a yellow liquid containing a faintly yellowish crystalline solid. The solid was separated by filtration, washed several times with pentane and dried *in vacuo* at 30–40°. The PMR spectrum of a solution of this solid (m.p. 156–159°) in dimethyl sulphoxide revealed the presence of phenyl groups, ethyl groups and HMPT, the integrated ratios of which corresponded with the structure $[\text{Ph}_3\text{BGeEt}_3]\text{-Li}\cdot 4\text{ HMPT}$.

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REFERENCES

- 1 E. J. BULTEN AND J. G. NOLTES, *J. Organometal. Chem.*, 29 (1971) 397.
- 2 C. A. KRAUS AND L. S. FOSTER, *J. Amer. Chem. Soc.*, 49 (1927) 457.
- 3 E. J. BULTEN AND J. G. NOLTES, *Tetrahedron Lett.*, (1967) 1443.
- 4 O. W. STEWARD AND J. E. DZIEDZIC, *J. Organometal. Chem.*, 16 (1969) P5.
- 5 A. G. BROOK, *J. Amer. Chem. Soc.*, 77 (1955) 4827.
- 6 A. G. BROOK AND H. GILMAN, *J. Amer. Chem. Soc.*, 77 (1955) 2322.
- 7 N. S. VYAZANKIN, E. N. GLADYSHEV, G. A. RAZUVAEV AND S. P. KORNEVA, *Zh. Obshch. Khim.*, 36 (1966) 952; *Chem. Abstr.*, 65 (1966) 8955.

- 8 N. S. VYAZANKIN, G. A. RAZUVAEV, E. N. GLADYSHEV AND S. P. KORNEVA, *J. Organometal. Chem.*, 7 (1967) 353.
- 9 L. C. WILLEMSSENS AND G. J. M. VAN DER KERK, *Investigations in the field of organolead chemistry*, Inst. Org. Chem. TNO, Utrecht, ILZRO, New York, 1965, p. 42; *J. Organometal. Chem.*, 23 (1970) 471.
- 10 D. BLAKE, G. E. COATES AND J. M. TATE, *J. Chem. Soc.*, (1961) 618.
- 11 D. A. NICHOLSON, Ph. D. Thesis, *Dissertation Abstr.*, 26 (1965) 3026.
- 12 N. S. VYAZANKIN, E. N. GLADYSHEV, E. A. ARKHANGEL'SKAYA, G. A. RAZUVAEV AND S. P. KORNEVA, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1968) 2081; *Chem. Abstr.*, 70 (1969) 29022q.
- 13 L. C. WILLEMSSENS AND G. J. M. VAN DER KERK, *Investigations in the field of organolead chemistry*, Inst. Org. Chem. TNO, Utrecht, ILZRO, New York, 1965, p. 51-55; *J. Organometal. Chem.*, 4 (1965) 34.
- 14 D. SEYFERTH, G. RAAB AND S. O. GRIM, *J. Org. Chem.*, 26 (1961) 3034.
- 15 M. LESBRE, J. SATGÉ AND M. MASSOL, *C.R. Acad. Sci. Paris, Ser. C*, 258 (1964) 2842.
- 16 P. MAZEROLLES, M. LESBRE AND D. HUY-GIAO, *C.R. Acad. Sci. Paris, Ser. C*, 253 (1961) 673.
- 17 J. SATGÉ, *Ann. Chim.*, (1961) 34.
- 18 YU. I. BAUKOV, G. S. BURLACHENKO, I. YU. BELAVIN AND I. F. LUTSENKO, *Zh. Obshch. Khim.*, 36 (1966) 153; *Chem. Abstr.*, 64 (1966) 14213.

J. Organometal. Chem., 29 (1971) 409-417