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# SYNTHESES AND REACTIONS OF TRIETHYLGERMYLLITHIUM, -SODIUM, -POTASSIUM, -RUBIDIUM AND -CAESIUM IN WEAK SOLVATING SOLVENTS

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## Summary

Germylmetallic compounds, $Et_3GeM$, where M = Li, Na, K, Rb and Cs, have been prepared in high yield in n-hexane or benzene by the reaction of bis(triethylgermyl)mercury with the appropriate alkali metal. Reactions of these compounds with trimethylchlorosilane afforded the coupled product $Et_3GeSiMe_3$. The interaction of $Et_3GeM$ with benzophenone, acetophenone and phenylacetylene has also been examined. The course of these reactions (i.e. the composition and the yields of the various products) is strongly dependent on the solvating ability of the solvent and the nature of the alkali metal M.

## Introduction

It is well known that all methods of syntheses of organosilylmetallic compounds, $R_3SiM$, where M = alkali metal [1-3], and of their germanium analogues [4,5] are based on the use of solvating solvents such as diethyl ether (a poor solvating agent [6]), tetrahydrofuran (a strong solvating agent) or 1,2-dimethoxyethane and hexamethylphosphotriamide (HMPT) (very strong solvating agents) etc.

Recently we have proposed a new method for the synthesis of trialkylsilyl- and trialkylgermyl-lithium compounds [7,8]. According to this method, the lithium derivatives may be obtained not only in polar solvents (e.g. THF) but also in solvents such as hexane, which have no specific solvating power:

$$(R_3M)_2Hg + 2Li \xrightarrow[\text{or benzene}]{\text{hexane}} 2R_3MLi + Hg \qquad (1)$$

[R = Et or i-Pr; M = Si, Ge]

As a result it is now possible to study the influence of the nature of the solvent on the stability and reactivity of trialkylsilylmetallic and trialkylgermylmetallic compounds.

A few examples may serve to indicate the considerable influence of the solvent and the nature of the alkali metal on the chemistry of silyl-, germyl- and stannyl-metallic compounds.

Thus it has been observed previously that trimethylstannyllithium is stable in THF, but attempted removal of this solvent by evaporation in vacuo even at −78° always leads to the decomposition of the $Me_3SnLi$ [9]. In contrast, when unsolvated, trimethylsilyllithium is completely stable and may be sublimed under high vacuum at 60° [10].

As reported recently [11] reaction of $Et_3GeLi$ in benzene with benzophenone gives rise to the formation of (triethylgermyl)diphenylmethanol, i.e. the normal product of addition to a carbonyl group. On the other hand, $Et_3GeK$ reacts with benzophenone in HMPT via an electron-transfer process and intermediate ketyl formation [12].

Evans et al. [13] have examined the spectra of $Ph_3Si^-M^+$, where M = Li, Na, K, Rb and Cs, and the reactions of these compounds with 1,1-diphenylethylene in THF. They concluded that solvated ion pairs are in contact in the case of sodium, potassium, rubidium and caesium, but that for $Ph_3Si^-Li^+$ contact ion pairs and solvent-separated ion pairs exist in equilibrium. Finally, it is also known [14] that the stereochemistry of the reaction of $R_3SnM$ compounds (M = Li, Na, K) with organic halides is strongly influenced by the nature of the solvent and of the alkali metal counter-ion in the stannylmetallic compound.

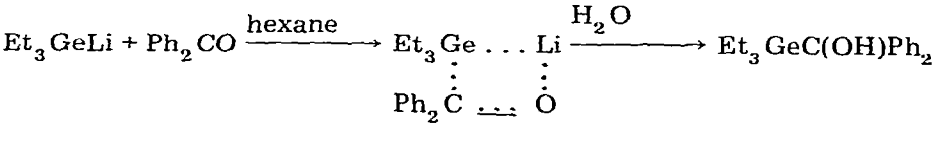
## Results and discussion

Trialkylgermylmetallic compounds $R_3GeM$, where M = Na, K, Rb and Cs, may be obtained via reaction (1) using n-hexane, benzene or polar solvents.

In benzene the reaction of bis(triethylgermyl)mercury with sodium or potassium is complete at room temperature after ca. 4 h. Under comparable conditions, formation of triethylgermylrubidium and -caesium occurs within a few minutes.

A high yield of triethylgermylmetallic compounds is obtained as is illustrated by reactions with trimethylchlorosilane which lead to trimethylsilyltriethylgermane, $Et_3GeSiMe_3$, (82—87%). Still greater yields (97%) of $Et_3GeSiMe_3$ are obtained in the reaction of $Et_3GeRb$ with $Me_3SiCl$ in THF.

It has been established that the course of the reaction between triethylgermylmetallic compounds and benzophenone is determined by the solvating ability of the solvent. Thus, triethylgermyllithium in n-hexane gives a 79% yield of (triethylgermyl)diphenylmethanol at room temperature, a result which may be interpreted in terms of a nucleophilic attack of the $Et_3Ge^-$ anion at the carbonyl carbon:



$$Et_3GeLi + Ph_2CO \xrightarrow{\text{hexane}} \begin{array}{c} Et_3Ge \ldots Li \\ \vdots \qquad \vdots \\ Ph_2C \ldots O \end{array} \xrightarrow{H_2O} Et_3GeC(OH)Ph_2 \qquad (2)$$

The yield of hexaethyldigermane as a by-product is only 7.0%. In the more strongly solvating solvent benzene, the yield of the carbinol is decreased to 60%.

Finally, when the same reaction is carried out in benzene in the presence of the strongly basic solvent HMPT (e.g. at a molar ratio of $Et_3GeLi/Ph_2CO/HMPT = 1/1/1$), reaction (2) is strongly suppressed (see Table 1). In this case, the existence of the corresponding paramagnetic ketyl was demonstrated by its ESR spectrum and (after hydrolysis) hexaethyldigermane, benzophenone and diphenylmethanol were obtained (ref. 12).

This result demonstrates that the reaction proceeds by means of a one-electron transfer mechanism. The ESR spectrum contains a complex multiplet due to splitting involving an unpaired electron on the *o*-, *m*- and *p*-protons of the two benzene rings of the radical. The hyperfine coupling constants ($a_H^p = 3.6$ G, $a_H^o = 2.7$ G, $a_H^m = 0.9$ G) and the relative line intensities are in good agreement with data recorded in the literature [15].

A strong solvent effect is also observed in the reaction of benzophenone with triethylgermylpotassium (see Table 1).

In attempting to explain these facts, account should be taken of the fact that the optically active ethyl(1-naphthyl)phenylgermyllithium reacts with ketones (for example, with benzophenone) in diethyl ether by means of a reaction similar to that given in equation (2) with retention of configuration [16]. The stereospecificity of such reactions indicates a large degree of association between the $R_3Ge$ anion and the lithium cation in the resulting ion pair [4], and hence the possibility of a four-centre molecular mechanism for these reactions [16].

However, on going from poorly solvating to very strongly solvating solvents, the possibility arises that the tightly bound ion pairs, which react preferentially by means of a four-centre mechanism [see equation(2)], are replaced by more "free" ion pairs (e.g. solvent-separated ion pairs) or in the extreme case by a virtually ionic structure.

Thus, for example, ionic structures are very probable for trialkylgermyl-

TABLE 1

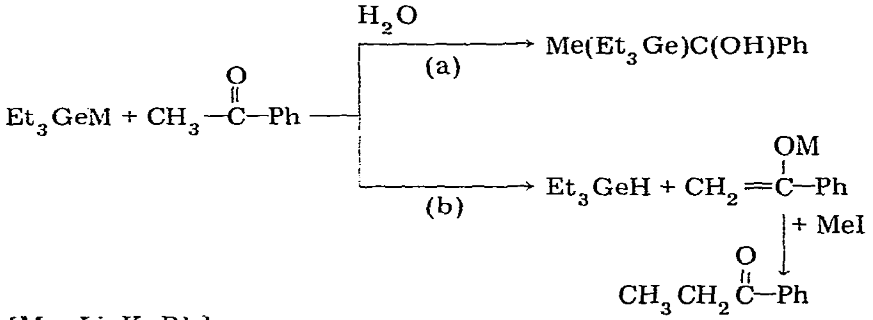
REACTION OF TRIETHYLGERMYL ALKALI METAL COMPOUNDS WITH BENZOPHENONE

| Reactants | | Solvent (ml) | Reaction products [g (%)] | | | |
|---|---|---|---|---|---|---|
| $Et_3GeM$ (mmole) | $Ph_2CO$ [g(mmole)] | | $Ph_2\underset{\displaystyle GeEt_3}{\underset{\vert}{C}}(OH)$ | $Et_6Ge_2$ | $Ph_2CO$ | $Ph_2CHOH$ |
| $Et_3GeLi$<br>14.16 | 2.91<br>(15.97) | hexane<br>25 | 3.82<br>(79) | 0.16<br>(7) | 0.41<br>(3) | |
| $Et_3GeLi$<br>3.90 | 0.72<br>(3.95) | benzene<br>20 | 0.80<br>(60) | 0.04<br>(7) | 0.20<br>(27) | |
| $Et_3GeLi$<br>12.00 | 2.20<br>(12.07) | benzene<br>20<br>HMPT [a] | | 1.35<br>(70) | 1.20<br>(54) | 1.06<br>(48) |
| $Et_3GeK$<br>11.00 | 2.10<br>(11.53) | benzene<br>25 | 2.57<br>(68) | 0.12<br>(7) | | |
| $Et_3GeK$<br>14.26 | 2.68<br>(14.82) | benzene<br>25<br>HMPT [a] | 0.10<br>(2) | 1.60<br>(70) | 1.40<br>(54) | 0.94<br>(36) |

[a] HMPT was used in equimolar quantities with the initial reactants.

metallic compounds in HMPT, and such a dramatic change in the structure of the germylmetallic compounds naturally has a considerable effect on their chemical properties. Hence it is known that thermal decomposition of $Et_3GeK$ in HMPT may occur via a one-electron transfer mechanism since the solvent molecules act as electron acceptors [5]. Benzophenone is a stronger electron acceptor then HMPT, however, and this may explain the readiness with which ketyl formation occurs in reactions involving trialkylgermylmetallic compounds in this solvent.

Reaction of triethylgermylmetallic compounds with acetophenone in benzene involves two competing processes: (i) nucleophilic attack of the $Et_3Ge$ anion at the carbonyl carbon [equation (3a)], and (ii) metallation of acetophenone [equation (3b)]



(3)

[M = Li, K, Rb]

The relative importance of these two processes is governed essentially by the nature of the metallic cation M associated with the $Et_3Ge$ anion (see Table 2). Thus, use of a lithium reagent favours the nucleophilic reaction (3a) at the carbon atom, the yield of the resulting 1-phenyl-1-(triethylgermyl)ethanol being 70%. In contrast, α-hydrogen abstraction [equation (3b)] is favoured to a much greater extent by germylpotassium and germylrubidium derivatives in

TABLE 2

REACTIONS OF TRIETHYLGERMYL ALKALI METAL COMPOUNDS WITH ACETOPHENONE

| Reactants | | Solvent (ml) | Reaction products [g (%)] | |
|---|---|---|---|---|
| $Et_3GeM$ (mmole) | MeCOPh [g(mmole)] | | $Me(Et_3Ge)C(OH)Ph$ [a] | $Et_3GeH$ |
| $Et_3GeLi$<br>25.32 | 3.30<br>(27.47) | benzene<br>25 | 5.00<br>(70) | 1.10<br>(27) |
| $Et_3GeLi$<br>16.36 | 1.90<br>(15.81) | benzene<br>20<br>HMPT [b] | 1.80<br>(41)[c] | 1.22<br>(48)[c] |
| $Et_3GeK$<br>11.76 | 1.46<br>(12.15) | benzene<br>20 | 0.15<br>(5) | 1.40<br>(74) |
| $Et_3GeRb$<br>11.36 | 1.63<br>(13.57) | benzene<br>20 | traces | 1.80<br>(99) |

[a] B.p. 107—108°C/1 mmHg, $n_D^{20}$ 1.5220. (Found: C, 59.26; H, 8.39; $H_{act.}$, 0.34%. Calculated for $C_{14}H_{24}GeO$: C, 59.85; H, 8.61; $H_{act.}$, 0.36%.)

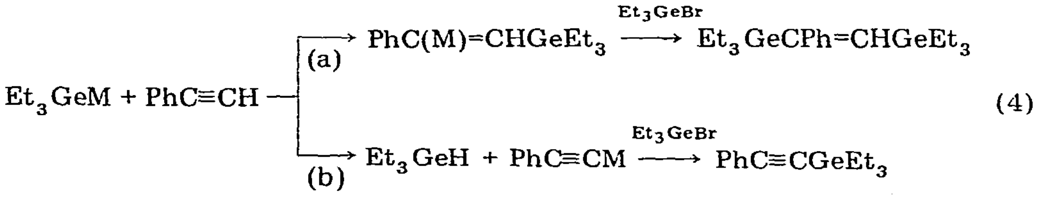
[b] HMPT was used in equimolar quantities relative to the initial reactants.

[c] The yields of products were calculated in terms of the initial amount of acetophenone.

comparison to germyllithium species (see also ref. 5). In these cases triethylgermane is obtained in a 74-99% yield. This observation was by treatment of the resulting reaction mixtures with methyl iodide and subsequent gas chromatographic estimation of the amount of EtCOPh formed (65-86% yield). As can be seen in Table 2, addition of HMPT to benzene solutions increases the yield of metallation products (e.g. $Et_3GeH$) because of the reduction in the carbinol yield.

O'Sullivan et al. [17] have observed similar dependences in the reaction of acetophenone with phenyl alkali metal compounds $C_6H_5M$, where M = Li, Na and K. It has been suggested [17,18] that as the atomic number of the alkali metal increases the compounds PhM and $Et_3GeM$ become stronger bases, attacking mainly at the α-hydrogen atom of acetophenone. On the other hand, the compounds PhLi and $Et_3GeLi$ are stronger nucleophiles than their corresponding analogues and attack the carbonyl carbon atom.

The reaction of triethylgermylmetallic compounds with phenylacetylene in benzene also involves to concurrent processes.



$$Et_3GeM + PhC\equiv CH \begin{cases} \xrightarrow{(a)} PhC(M)=CHGeEt_3 \xrightarrow{Et_3GeBr} Et_3GeCPh=CHGeEt_3 \\ \xrightarrow{(b)} Et_3GeH + PhC\equiv CM \xrightarrow{Et_3GeBr} PhC\equiv CGeEt_3 \end{cases} \qquad (4)$$

[M = Li, K]

It is known that triethylgermyllithium adds at the double bond of ethylene and its homologues [7,11], styrene and diphenylacetylene [11] under relatively mild conditions. However, reaction of $Et_3GeLi$ with phenylacetylene in benzene proceeds generally according to 4(b), giving the metallation products. The yields of triethylgermane and 1-(triethylgermyl)-2-phenylacetylene [equation (4b)] are 57 and 54%, respectively, whereas the yield of the adduct [equation (4a)] is only 39%. If the reaction is carried out in benzene in the presence of HMPT (for example, at the molar ratio $PhC=CH/Et_3GeLi/HMPT$ = 1/1/1), reaction (4a) is suppressed completely. Reaction of phenylacetylene with $Et_3GeK$ in benzene follows path 4(b) similarly. We have shown previously [19] that triethylgermylmetallic compounds, $Et_3GeM$, react with ethylene, the yield of the adduct decreasing on going from lithium to sodium and potassium compounds.

Addition of HMPT to the various reaction systems studied thus considerably decreases the yields of adducts obtained in reactions (2), (3a) and (4a). It can be assumed (see ref. 18) that the formation of such adducts is preceded by formation of a donor-acceptor complex in which the triethylgermyllithium acts as a Lewis acid and benzophenone (or acetophenone or phenylacetylene) acts as an electron-pair donating molecule; HMPT, however, inhibits such complex formation since it is a stronger Lewis base than $Et_3GeLi$.

## Experimental

All reactions involving triethylgermyl alkali metal compounds were performed in evacuated sealed ampoules ensuring that all oxygen and moisture were excluded. GLC analyses were made by means of a "Tsvet-4" chromatograph with a heat conductivity detector, using helium as the carrier gas and employing a 100 × 0.4 cm column packed with Apiezon L (15%) on Chromaton H—AB.

### *Triethylgermylcaesium*

Caesium (2.12 g, 0.01695 g atom) (in the form of a Cs mirror) was placed in an ampoule, a solution of bis(triethylgermyl)mercury (4.19 g, 8.05 mmole) in 20 ml of benzene added and the ampoule evacuated and sealed. An exothermal reaction occurred at ca. 20°C which was completed in 3—5 min giving a dark-red solution of triethylgermylcaesium together with metallic mercury (1.37 g, 85%). Triethylgermylrubidium was prepared analogously.

### *Reaction of triethylgermylcaesium with trimethylchlorosilane*

Trimethylchlorosilane (3 ml; excess) was added at ca. 20° to a solution of triethylgermylcaesium (7.7 mmole) prepared in the manner described above. After 3—5 min the mixture was completely decoloured and caesium chloride (1.14 g, 88%) was precipitated. The organic layer was separated and the solvent removed under reduced pressure. GLC analysis of the residue obtained revealed the presence of trimethylsilyltriethylgermane (1.50 g, 84%).

Using similar conditions, 5.98 mmole of triethylgermylrubidium, 6.78 mmole of triethylgermylpotassium and 7.18 mmole of triethylgermylsodium respectively with excess trimethylchlorosilane in benzene gave trimethylsilyltriethylgermane in yields of 82, 82 and 87%.

### *Reaction of triethylgermyllithium with benzophenone in hexane*

Triethylgermyllithium (14.16 mmole) in 20 ml of hexane was added to a solution of benzophenone (2.91 g, 15.97 mmole) in 10 ml of hexane and the mixture was allowed to stand overnight at ca. 20°C. The resulting dark-red reaction mixture was then decomposed with water, the organic layer separated, dried over $MgSO_4$ and evaporated. GLC analysis of the residue obtained indicated the presence of triethylgermyldiphenylcarbinol (3.82 g, 79%), hexaethyldigermane (0.16 g, 7%) and benzophenone (0.41 g, 3%).

### *Reaction of triethylgermylpotassium with benzophenone in benzene with addition of HMPT*

HMPT (2.68 g, 14.71 mmole) was added to 14.26 mmole of triethylgermylpotassium in 25 ml of benzene. The resulting red-orange mixture was added to benzophenone (2.70 g, 14.82 mmole) in 5 ml of benzene. A bright blue colour immediately appeared indicating the presence of paramagnetic benzophenone ketyl. The ketyl was identified by its ESR spectrum, registered on a commercial radiospectrometer Rz-1301. GLC analysis of the reaction mixture (column 100 × 0.4 cm, packed with OV 225 (15%) on Silochrom, at He flow rate 31 ml·min$^{-1}$ and 220°) showed hexaethyldigermane (1.60 g 70%), benzophenone (1.40 g, 54%), diphenylcarbinol (0.94 g, 36%) and triethylgermyldiphenylcarbinol (0.10 g, 2%).

Other runs were carried out analogously (see Table 1).

### *Reaction of triethylgermylrubidium with acetophenone in benzene*

The red-brown solution of triethylgermylrubidium (11.36 mmole) in 20 ml of benzene was added to a solution of acetophenone (1.63 g, 13.57 mmole) in 5 ml of benzene. After standing at ca. 20° for 3-5 min, the colour disappeared and a colourless rubidium enolate was precipitated. The organic layer was separated and subsequently GLC analyses showed the presence of triethylgermane (1.80 g, 99%) and traces of acetophenone and 1-phenyl-1-(triethylgermyl)ethanol. A solution of methyl iodide (excess) in benzene was added to the precipitate of rubidium enolate at ca. 20°. Rubidium iodide (1.93 g, 80%) was obtained. GLC analysis of the organic phase showed the presence of ethyl phenyl ketone (1.31 g, 86%).

### *Reaction of triethylgermyllithium with phenylacetylene in benzene*

A solution of triethylgermyllithium (7.70 mmole) in benzene was added to phenylacetylene (0.80 g, 7.80 mmole) in 5 ml of benzene. White solid $PhC{\equiv}CLi$ was precipitated, the resulting organic layer being red in colour. At ~ 20° the reaction was completed in 3-5 min. Triethylgermane (0.70 g, 57%) was shown to be present in the organic layer (GLC) along with traces of phenylacetylene. The mixture was treated with excess triethylbromogermane, and the solid dissolved and the colour of the organic layer disappeared. After removal of the solvent, 1,2-bis(triethylgermyl)-1-phenylethylene (1.25 g, 39%), 1-triethylgermyl-2-phenylacetylene (1.25 g, 54%) and the traces of hexaethyldigermane were identified in the residue by the usual procedure.

In a similar manner, 10.96 mmole of triethylgermyllithium in hexane and phenylacetylene (1.30 g, 12.73 mmole) in 5 ml of hexane gave triethylgermane (1.12 g, 64%). After treatment of the reaction mixture with excess triethylbromogermane (3 ml), the products were identified by the methods used previously, as 1,2-bis(triethylgermyl)-1-phenylethylene (0.92 g, 20%), 1-triethylgermyl-2-phenylacetylene (1.74 g, 61%) and traces of hexaethyldigermane.

### *Reaction of triethylgermyllithium with phenylacetylene in benzene in the presence of HMPT*

To a benzene solution of triethylgermyllithium (4.29 mmole), an equimolar amount of HMPT was added. The resulting mixture was added to phenylacetylene (0.44 g, 4.31 mmole) and the solution became dark-red in colour after 3 - 5 min at ca. 20°. GLC analysis of the mixture showed the existence of triethylgermane (0.47 g, 68%). Addition of excess $Et_3GeBr$ (3 ml) and removal of the solvent led to 1-triethylgermyl-2-phenylacetylene (1.06 g, 95%) (GLC analysis) and traces of phenylacetylene and hexaethyldigermane.

### *Reaction of triethylgermylpotassium with phenylacetylene in benzene*

A benzene solution of triethylgermylpotassium (11.06 mmole) was added to phenylacetylene (1.18 g, 11.56 mmole) in 5 ml of benzene. The resulting reaction was complete after 3 - 5 min at ca. 20°. A considerable quantity of

PhC≡CK was formed as a white solid. After removal of the solid, GLC analysis of the colourless organic phase showed the presence of triethylgermane (1.45 g, 82%). The residue was treated with excess methyl iodide (10 ml) when potassium iodide (1.61 g, 88%) was precipitated. GLC analysis of the organic layer revealed the presence of $PhC{\equiv}CCH_3$ (0.90 g, 70%).

## References

1 H. Gilman and H.I.S. Winkler, in H. Zeiss (Ed.), Organometallic Chemistry, Reinhold, New York, 1960, p. 270.
2 S.N. Borisov, M.G. Voronkov and E.Ya. Lukevits, in E.G. Rochow (Ed.), Organosilicon Heteropolymers and Heterocompounds, Plenum Press, New York, 1970.
3 H. Sakurai, A. Okada, M. Kira and K. Yonezawa, Tetrahedron Lett., (1971) 1511.
4 D.D. Davis and C.E. Gray, Organometal. Chem. Rev. A, 6 (1970) 283.
5 E.J. Bulten and J.G. Noltes, J. Organometal. Chem., 29 (1971) 397.
6 J.W. Burley and R.N. Young, J. Chem. Soc. B,(1971) 1018.
7 N.S. Vyazankin, G.A. Razuvaev, E.N. Gladyshev and S.P. Korneva, J. Organometal. Chem., 7 (1967) 353.
8 N.S. Vyazankin, G.A. Razuvaev and O.A. Kruglaya, Organometal. Chem. Syn., 1 (1971) 205.
9 W.L. Wells and T.L. Brown, J. Organometal. Chem., 11 (1968) 271.
10 T.F. Schaaf and J.P. Oliver, J. Amer. Chem. Soc., 91 (1969) 4327.
11 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.
12 E.J. Bulten and J.G. Noltes, J. Organometal. Chem., 29 (1971) 409.
13 A.G. Evans, M.L. Jones and N.H. Rees, J. Chem. Soc., Perkin Trans. II, (1972) 389.
14 H.G. Kuivila, J.L. Considine and J.D. Kennedy, J. Amer, Chem. Soc., 94 (1972) 7206.
15 V.M. Kazakov, G.M. Lipkind, I.G. Makarov, B.I. Shapiro and Ya.K. Syrkin, in Radiospektroskopicheskie i kvantovokhimicheskie metody v strukturnykh issledovaniyakh, "Nauka", Moscow, 1967, p. 99.
16 C. Eaborn, R.E.E. Hill and P. Simpson, J. Organometal. Chem., 37 (1972) 267.
17 W.I. O'Sullivan, F.W. Swamer, W.Y. Humphlett and C.R. Hauser, J. Org. Chem., 26 (1961) 2306.
18 R.A. Finnegan, Ann. N.Y. Acad. Sci., 159 (1969) 242.
19 E.N. Gladyshev, E.A. Fedorova, N.S. Vyazankin and G.A. Razuvaev, Zh. Obshch. Khim., 43 (1973) 1315.