ORGANOSILICON COMPOUNDS
XLVIII*. EFFECTS OF α-TRIMETHYLSILYL GROUPS ON RATES OF REACTION AT CARBON–HALOGEN BONDS

M. A. COOK, C. EABORN AND D. R. M. WALTON

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received January 4th, 1971)

SUMMARY

The compounds $(Me_3Si)_xCH_{(3-x)}Cl$ ($x=1$–3), $(Me_3Si)_xCH_{(3-x)}Br$ ($x=1, 3$) and Me_3SiCMe_2Br have been found to react with 90% acetone or 80% ethanol at 70° at rates too small for convenient measurement. Towards aqueous acetone, the compound $PhMe(Me_3Si)CBr$ is 110 times less reactive at 50° than $PhMe_2CBr$ at 0°. It is concluded that relative to α-Me, α-t-Bu or α-H, α-Me_3Si groups decrease the ease of formation of carbonium ions.

Second-order rate constants have been determined for the reaction of $(Me_3Si)_x$-$CH_{(3-x)}Hal$ compounds and of Me_3SiCMe_2Br with sodium ethoxide in ethanol at 70°, and indicate that the α-Me_3Si groups have a fairly small deactivating effect relative to the α-Me group in these reactions. Thus the compound Me_3SiCMe_2Cl is 5.6 times as reactive as $(Me_3Si)_3CCl$. The rates of reaction of the $(Me_3Si)_xCH_{(3-x)}Cl$ compounds with $x=1$, 2, and 3, respectively, fall in the ratios 4.8/1.2/1.0.

INTRODUCTION

We have previously studied several aspects of the effects of trimethylsilyl groups on the reactivity of organic systems. For example, we have recently shown that the compound $(Me_3Si)_3CH$ can be readily metalated to give an unusually stable lithium derivative $(Me_3Si)_3CLi$, an effect which can be plausibly attributed[2], at least in part, to the stabilising effect of $(p–d)_\pi$-bonding between the carbanion centre and the adjacent silicon atom. Similarly we have shown that the free radical $(Me_3Si)_3C\cdot$ is exceptionally stable[3], and once again $(p–d)_\pi$ interaction probably contributes to the stabilisation. In both cases, however, steric effects must be substantial. Much earlier we showed that the trimethylsilylmethyl chloride, Me_3SiCH_2Cl, was more reactive than ethyl chloride towards nucleophilic substitution by iodide ion in acetone and suggested that this effect of the Me_3Si group might be associated with a bridging mechanism involving interaction of the entering iodide ion with the vacant d-orbitals of the silicon atom[4]. Such an effect was assumed to overcome the deactivation

---

* For Part XLVII see ref. 1.

expected to be brought about by the inductive effect of the Me_3Si group, which is normally thought to involve electron release from silicon to a saturated carbon atom. In aqueous ethanol, iodide exchange occurs less readily with Me_3SiCH_2I than CH_3CH_2I[5], and it could be that more effective solvation of the entering and leaving halide ions in this medium both sterically hinders bridging and reduces the need for it, so that the deactivating influence of the inductive effect of the Me_3Si group predominates. The compound Me_3SiCH_2Cl is also less reactive than CH_3CH_2Cl towards ethoxide ion in ethanol[6], and again the bridging mechanism may be inoperative, possibly because of the solvation effect mentioned above coupled with the poorer bridging ability of ethoxide ion.

We have not previously studied the effects of Me_3Si groups on an adjacent carbonium ion centre, although we have drawn attention to the apparent anomaly presented by the observation that the compounds Me_3SiCH_2X (X = Cl, I) do not react with silver nitrate in ethanol under conditions in which the corresponding n-hexyl halides react readily, in spite of the fact that inductive electron release by the Me_3Si group should assist this reaction by stabilising the forming carbonium ion[7]. The deactivating effect of the Me_3Si group cannot easily be associated with steric hindrance to solvation of the carbonium ion because neopentyl halides, Me_3CCH_2X, for which the hindrance should be markedly greater, are normally reactive[8]. We now describe studies of the effects of α-Me_3Si groups on the ease of neutral solvolysis of some alkyl chlorides and bromides; the results indicate that the groups have a substantial deactivating effect on carbonium-ion forming reactions. We also present data on the interaction of these halides with base in aqueous ethanol.

RESULTS AND DISCUSSION

The reactions with 90% aqueous acetone or 80% aqueous ethanol of all the compounds listed in Table 1 were found to be too slow to measure even at $-70°$: less than 5% of reaction occurred in 48 hours (i.e. $k_1 < 3 \times 10^{-7}$ sec^{-1}). Most significant is the very low reactivity of the halides Me_3SiCMe_2X, since the corresponding Me_3CX and Me_3CCMe_2X compounds react rapidly by the unimolecular (ionisation) mechanism in 80% aqueous ethanol under these conditions[8,*]. Thus introduction of

TABLE 1

RATES OF REACTION OF α-(TRIMETHYLSILYL)ALKYL HALIDES AT 70.0°

Compound	NaOEt (ca. 0.45 M) in EtOH $10^5 k_2$ (l·mole^{-1}·sec^{-1})	90% acetone or 80% EtOH
Me_3SiCH_2Cl	1.2	
$(Me_3Si)_2CHCl$	0.30	
$(Me_3Si)_3CCl$	0.25	
Me_3SiCMe_2Cl	1.4	No detectable reaction
Me_3SiCH_2Br	12.5	$k_1 < 3 \times 10^{-7}$ sec^{-1}
$(Me_3Si)_3CBr$	0.92	
Me_3SiCMe_2Br	20	

* In these latter reactions both elimination and substitution products are formed, but this does not affect the rate of formation of carbonium ions.

an Me_3Si group in place of either an Me or an Me_3C group leads to a considerable fall in the ease of reaction by the ionisation mechanism, and steric hindrance to solvation of the carbonium ion does not provide an acceptable explanation, since an Me_3C group offers even greater hindrance. It thus seems that the Me_3Si group is less able to stabilise an adjacent carbonium ion centre through electronic effects than are Me or Me_3C groups; this cannot be taken, however, to imply that the Me_3Si group has the smallest electron-releasing inductive effect, since the stabilising effects of the Me and Me_3C groups may be mainly due to electron release by C–H and C–C hyperconjugation*.

The low reactivity of the compound Me_3SiCMe_2Br in the neutral solvolysis also means that the Me_3Si group has a deactivating effect relative to hydrogen, since isopropyl bromide, $HCMe_2Br$, reacts fairly readily in the medium used, and mainly by a unimolecular process; for example, the first order rate constant for the substitution reaction of isopropyl bromide in 80% ethanol[8] is 240×10^{-7} sec^{-1} at 55°, whereas the overall first order rate constant for disappearance of the compound Me_3SiCMe_2Br is $< 3 \times 10^{-7}$ sec^{-1} even at 70°. It seems rather unlikely that the group is actually electron-withdrawing relative to hydrogen, and we can offer no satisfactory explanation of the deactivation. It may possibly be associated with steric hindrance to solvation of the potential carbonium ion, but this would have to outweigh the accelerating effect associated with release of internal strain on passing from the tetrahedral to the planar trigonal structure. The absence of any detectable solvolysis of the halides $(Me_3Si)_3CX$ is in line with the other results, although a combination of potential steric acceleration with inductive electron release by the Me_3Si group might possibly have been expected to induce detectable S_N1 reactivity.

Consistently, the compound $PhMe(Me_3Si)CBr$ reacts with 90% aqueous acetone at 50° some 110 times as slowly as $PhMe_2CBr$ at 0° (see Table 2). This

TABLE 2

RATES OF REACTION OF α-(TRIMETHYLSILYL)BENZYL BROMIDES

Compound	Temp. (°C)	Medium	$10^7 k_1$ (sec^{-1})
PhMe$_2$CBr	0	90% acetone	1.9
PhMe(Me$_3$Si)CBr	50	90% acetone	0.0165
	50	80% ethanol	0.16

substantial reduction in reactivity (probably involving a factor of over 2000) on replacing an Me by an Me_3Si group may, however, be associated in part with steric interaction between the Me_3Si group and the o-hydrogen atom of the Ph group in the carbonium ion, which prevents the benzene ring from becoming co-planar with the three bonds to the carbonium ion centre and thus reduces the conjugative stabilisation. [Such an effect has been postulated to explain the fact that Ph(t-Bu)CHCl is

---

* Analogous hyperconjugation from the SiMe$_3$ group is somewhat inhibited by the greater length of the C–SiMe$_3$ bond, and would also require contributions from relatively unfavourable structures such as C=SiMe$_2$ CH$_3^+$; hyperconjugation involving structures such as C=C SiMe$_3^+$, on the other hand, can be of major importance when the Me$_3$Si group is β to a C–Hal bond[9].

markedly less reactive than PhMeCHCl in neutral solvolysis[10].] The compounds Ph(Me₃Si)HCBr and Ph(Me₃Si)₂CBr do not react with 90% acetone or 80% ethanol at a measurable rate at 70°, but do give a precipitate of silver bromide when refluxed with ethanolic silver nitrate for 5 minutes.

    The rate constants for second-order reactions of some of the compounds with sodium ethoxide in ethanol are also shown in Table 1. The introduction of additional α-Me₃Si groups, in the series $(Me_3Si)_xCH_{(3-x)}X$ with $x = 1-3$, causes a small lowering of the reactivity, the effect being most marked for the change $x=1$ to $x=2$. This lowering of reactivity may be more the result of steric hindrance than of additional electron supply to the central carbon atom. Indeed, it is somewhat surprising that the reactivity falls so little on introduction of the third Me₃Si group, but we must emphasise that we did not examine the products of the reaction, and it is possible that rearrangements or Me₃Si–C bond cleavages occur in the case of the $(Me_3Si)_xCH_{(3-x)}X$ compounds with $x=2$ and 3. The reactions of Me₃SiCMe₂X probably mainly involve elimination; second-order rate constants of 0.295×10^{-5} and 9.7×10^{-5} sec⁻¹·mole⁻¹ have been recorded for the combined E2 and S_N2 reactions of isopropyl bromide under similar conditions at 25° and 55°, respectively[11], and extrapolation gives a total rate constant of 125×10^{-5} sec⁻¹·mole⁻¹ at 70°, compared with that of 20×10^{-5} observed for Me₃SiCMe₂Br. All that can be concluded from this rough comparison is that the effect of replacing a secondary hydrogen atom of isopropyl bromide by a trimethylsilyl group is not very large, which is consistent with the influence of the group on the bimolecular reactions of the other compounds studied.

EXPERIMENTAL

(Bromomethyl)trimethylsilane

    (Bromomethyl)dimethylchlorosilane (61 g, 0.30 mole), prepared by radical bromination of chlorotrimethylsilane[12], was treated with methylmagnesium bromide (0.25 mole) in ether (450 ml). The mixture was boiled under reflux for 4 h, then added to a slurry of ice and ammonium chloride. The ether layer was separated, dried (MgSO₄), and distilled to give (bromomethyl)trimethylsilane (41 g, 80%), b.p. 115°, n_D^{25} 1.4420 (lit.[12] b.p. 115.5°, n_D^{25} 1.4422). The ¹H NMR spectrum showed τ values as follows: (CH₃)₃Si, 9.87; CH₂Br, 7.58.

(Chloromethyl)trimethylsilane

    (Chloromethyl)dimethylchlorosilane (21 g, 0.15 mole), prepared by photochlorination of chlorotrimethylsilane[13], was treated with methylmagnesium bromide (0.13 mole) in ether (300 ml). The mixture was boiled under reflux for 4 h, then worked up in the usual way to give (chloromethyl)trimethylsilane (12 g, 49%), b.p. 97°, n_D^{25} 1.4150 (lit.[14] b.p. 97.1°, n_D^{20} 1.4180). The ¹H NMR spectrum showed τ values as follows: (CH₃)₃Si, 9.89; CH₂Cl, 7.28.

2-Chloro-2-(trimethylsilyl)propane

    (i). 2-(Trichlorosilyl)propane. The Grignard reagent prepared from isopropyl chloride (230 g, 3.0 moles) and magnesium turnings (72 g, 3.5 g-atom) in ether (900 ml) was slowly added to a solution of silicon tetrachloride (1000 g, 7.0 moles) in ether (200 ml), and the mixture was boiled under reflux for 12 h. Ether and residual

silicon tetrachloride were carefully fractionated from the reaction mixture, then the pressure was reduced and the crude product quickly distilled from the solid magnesium salts. Refractionation of this distillate gave 2-(trichlorosilyl)propane (250 g, 45%), b.p. 120° (lit.[15] b.p. 119°).

(ii). *1-Chloro-2-(trichlorosilyl)propane*. A mixture of 2-(trichlorosilyl)propane (250 g, 1.4 mole), sulphuryl chloride (200 g, 1.5 mole), and benzoyl peroxide (1 g) was boiled under reflux for 6 h, then fractionally distilled to give 2-chloro-2-(trichlorosilyl)propane (60 g, 20%), b.p. 151° (lit.[15] b.p. 151°), followed by 1-chloro-2-(trichlorosilyl)propane (190 g, 65%), b.p. 165° (lit.[15] b.p. 164°).

(iii). *2-(Trichlorosilyl)propene*. 1-Chloro-2-(trichlorosilyl)propane (190 g, 0.9 mole) was boiled under reflux with an excess of quinoline, and the crude dehydrohalogenation product was continuously distilled from the mixture. Refractionation of the distillate gave 2-(trichlorosilyl)propene (110 g, 75%), b.p. 113° (lit.[15] b.p. 113.5°).

(iv). *2-(Trimethylsilyl)propene*. 2-(Trichlorosilyl)propene (85 g, 0.50 mole) was added slowly to methylmagnesium bromide (2.0 moles) in ether (1000 ml). The mixture was boiled under reflux for 12 h, then treated with ice-water. The organic layer was separated and the aqueous layer extracted with ether. The combined organic phases were dried ($MgSO_4$) and distilled to give 2-(trimethylsilyl)propene (45 g, 75%), b.p. 82°, n_D^{25} 1.4065 (lit.[16] b.p. 82°, n_D^{20} 1.4061).

(v). *2-Chloro-2-(trimethylsilyl)propane*. A mixture of concentrated hydrochloric acid (150 ml) and 2-(trimethylsilyl)propene (15 g, 0.13 mole) was vigorously stirred at 60° for 24 h. Organic products were extracted with ether and the ether extract was dried and evaporated to give a solid. This was repeatedly crystallised from methanol and then resublimed *in vacuo* to give 2-chloro-2-(trimethylsilyl)propane (7.8 g, 40%), m.p. 95–97° (sealed tube) (lit.[17] m.p. 95–97°). The ^{1}H NMR spectrum showed τ values as follows: $(CH_3)_3Si$, 9.9; $C(CH_3)_2$, 8.5.

2-Bromo-2-(trimethylsilyl)propane

2-(Trimethylsilyl)propene (15 g, 0.13 mole) was saturated with dry hydrogen bromide, first at room temperature for 10 min, then at −70° for a further 6 h. The solid which formed was taken up in methanol. The solvent was partially removed under reduced pressure, and the resulting crude solid was repeatedly recrystallised from methanol and finally sublimed to give 2-bromo-2-(trimethylsilyl)propane (9 g, 33%), m.p. 125–126° (sealed tube) (lit.[18] m.p. 124°). The ^{1}H NMR spectrum showed τ values as follows: $(CH_3)_3Si$, 9.89; $C(CH_3)_2$, 8.45.

Bis(trimethylsilyl)chloromethane

n-Butyllithium (66 ml of 1.5 *M* solution in hexane), precooled to −78°, was added to a solution of bis(trimethylsilyl)dichloromethane[19] (22.9 g, 0.10 mole) in a mixture of THF (200 ml), light petroleum (20 ml, b.p. 40–60°), and ether (20 ml) at −110°. The mixture was kept at this temperature for 2 h, then ethanol (20 ml) was added. The mixture was allowed to warm to room temperature during 12 h, and then treated with ice water. Organic products were extracted with ether and the ether layer was worked up in the usual way and distilled to give bis(trimethylsilyl)chloromethane (14.5 g, 73%), b.p. 98°/60 mm, n_D^{25} 1.4470 (lit.[26] b.p. 178.5°, n_D^{20} 1.4499). The ^{1}H NMR spectrum showed τ values as follows: $(CH_3)_3Si$, 9.88; CH, 7.65.

Bromo- and chloro-tris(trimethylsilyl)methane

N-Bromosuccinimide (33 g, 0.21 mole), benzoyl peroxide (0.1 g) and tris-(trimethylsilyl)methane[20] (50 g, 0.21 mole) in CCl_4 (300 ml) were boiled together under reflux for 5 days. The mixture was then cooled, and succinimide and unreacted N-bromosuccinimide were removed by filtration. Solvent was evaporated from the filtrate under reduced pressure and the residual solid was recrystallised from methanol to give bromotris(trimethylsilyl)methane (48 g, 52%) m.p. 189–192° (sealed tube) (lit.[21] m.p. 190°). The ^1H NMR spectrum showed a sharp singlet at 9.82 τ.

The preparation of chlorotris(trimethylsilyl)methane has been described elsewhere[2].

Bromo(phenyl)(trimethylsilyl)methane

Benzyltrimethylsilane (32.8 g, 0.20 mole), N-bromosuccinimide (36 g, 0.2 mole), and carbon tetrachloride (200 ml) were boiled together under reflux for 24 h. Precipitated succinimide was filtered off and the filtrate distilled to give bromo(phenyl)-(trimethylsilyl)methane (34 g, 73%), b.p. 98°/4 mm, n_D^{25} 1.5358 (lit.[22] b.p. 98–99°/4 mm, n_D^{25} 1.5389. The ^1H NMR spectrum showed τ values as follows: $(CH_3)_3Si$, 9.85; CH, 5.69; C_6H_5, 2.7 (multiplet).

1-Bromo-1-phenyl-1-(trimethylsilyl)ethane

(i). *α-(Trimethylsilyl)styrene.* A mixture of α-bromostyrene (36.5 g, 0.20 mole) magnesium turnings (6.0 g, 0.25 mole), chlorotrimethylsilane (20 g, 0.185 mole), hydroquinone (1.0 g) and THF (150 ml) was boiled under reflux for 12 h. Treatment with ice-water followed by the normal work-up procedure culminating in fractional distillation gave α-(trimethylsilyl)styrene (13 g, 32%), b.p. 54°/3 mm (lit.[23] b.p. 52°/3 mm).

(ii). *1-Bromo-1-phenyl-1-(trimethylsilyl)ethane.* α-(Trimethylsilyl)styrene (17.6 g, 0.10 mole) was saturated with dry hydrogen bromide gas initially at room temperature for 10 min, then at −30° until there was no further gain in weight (ca. 4 h). The mixture was then distilled to give 1-bromo-1-phenyl-1-(trimethylsilyl)ethane (nc) (12 g, 47%), b.p. 57°/0.25 mm. (Found: C, 51.35; H, 6.7. $C_{11}H_{17}BrSi$ calcd.: C, 51.2; H, 6.6%.) The ^1H NMR spectrum showed τ values as follows: $(CH_3)_3Si$, 9.95; $C(CH_3)$, 7.85; C_6H_5, 2.7 (multiplet).

Bis(trimethylsilyl)(bromo)phenylmethane

A mixture of bis(trimethylsilyl)phenylmethane[20] (24 g, 0.10 mole), N-bromosuccinimide (17.8 g, 0.10 mole), and carbon tetrachloride (200 ml) was refluxed for 48 h. Succinimide was removed by filtration and the filtrate was distilled to give bis(trimethylsilyl)(bromo)phenylmethane (nc) (12.5 g, 40%), b.p. 110°/2 mm. (Found: C, 49.3; H, 7.5. $C_{13}H_{23}BrSi_2$ calcd.: C, 49.5; H, 7.4%.) The ^1H NMR spectrum showed τ values as follows: $(CH_3)_3Si$, 9.75; C_6H_5, 2.65 (singlet).

Kinetic studies

General. Absolute ethanol (commercial grade) was distilled from sodium and excess of ethyl phthalate before use.

Solvolysis by ethoxide ion in absolute ethanol. In a typical run, freshly cut sodium (ca. 1.0 g) was dissolved in ethanol (50–75 ml) in a 100 ml volumetric flask.

TABLE 3

SOLVOLYSIS OF BROMOTRIS(TRIMETHYLSILYL)METHANE[a] BY SODIUM ETHOXIDE[b] IN ETHANOL

Time (10^5 sec)	0.0088 M AgNO$_3$ needed (ml)	$10^7 k_2$[c] ($l \cdot mole^{-1} \cdot sec^{-1}$)
0	0.30	
36	4.2	8.31
72	6.5	9.43
108	10.4	9.37
144	13.0	9.46
180	15.1	9.61
216	17.0	9.49
252	18.5	9.46
288	19.9	9.61

[a] Initial concn. 0.0575 M. [b] Initial concn. 0.4581 M. [c] Rate constants have been corrected for medium expansion.

An accurately weighed sample of silylalkyl halide was added and the volume was made up to 100 ml at 20° with ethanol. The concentration of ethoxide ion in the mixture was then determined by titration against 0.1 M hydrochloric acid. Samples (5 ml) were sealed under nitrogen into Pyrex ampoules which were thermostatted at 70° and removed at appropriate intervals and stored at −80° until required. The liberated halide ion in each sample was determined by titration against silver nitrate[6,24]. Second-order rate constants, normally determined graphically, were corrected by an appropriate factor (1.061) to allow for ethanol expansion between 20° and 70°. The specimen run in Table 3, figures with point-by-point evaluation of the rate constants, refers to the solvolysis of bromotris(trimethylsilyl)methane.

The techniques described by Brown and his colleagues[25] were used for measuring rates of solvolysis in 90 wt.% aqueous acetone at 50° and at 0°. A similar procedure was adopted for solvolysis of 1-bromo-1-phenyl-1-(trimethylsilyl)ethane in 80 wt.% aqueous ethanol.

REFERENCES

1 M. A. COOK, C. EABORN, AND D. R. M. WALTON, J. Organometal. Chem., 23 (1970) 85.
2 M. A. COOK, C. EABORN, A. E. JUKES AND D. R. M. WALTON, J. Organometal. Chem., 24 (1970) 529.
3 A. R. BASSINDALE, A. J. BOWLES, M. A. COOK, C. EABORN, A. HUDSON, R. A. JACKSON, AND A. E. JUKES, Chem. Commun., (1970) 559.
4 C. EABORN AND J. C. JEFFREY, J. Chem. Soc., (1954) 4266.
5 V. B. MILLER, M. B. NEUMANN, A. V. SAVITSKII AND V. F. MIRONOV, Dokl. Akad. Nauk SSSR, 101 (1955) 495; Chem. Abstr., 50 (1956) 3217.
6 C. EABORN AND J. C. JEFFREY, J. Chem. Soc., (1957) 137.
7 C. EABORN, Organosilicon Compounds, Butterworths, London, 1960, p. 433.
8 C. K. INGOLD, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca and London, 2nd Edn., 1969, Chapter 7.

9 A. R. BASSINDALE, C. EABORN, D. R. M. WALTON AND D. J. YOUNG, *J. Organometal. Chem.*, 20 (1969)
    49; M. A. COOK, C. EABORN AND D. R. M. WALTON, *J. Organometal. Chem.*, 24 (1970) 301.
10 G. BADDELEY, J. CHADWICK AND H. T. TAYLOR, *J. Chem. Soc.*, (1954) 2405.
11 M. L. DHAR, E. D. HUGHES AND C. K. INGOLD, *J. Chem. Soc.* (1950) 2058; M. L. DHAR, E. D. HUGHES,
    C. K. INGOLD, A. M. M. MANDORV, G. A. MAW AND L. I. WOOLF, *J. Chem. Soc.*, (1950) 2093.
12 J. L. SPEIER, *J. Amer. Chem. Soc.*, 73 (1951) 826.
13 R. H. KRIEBLE AND J. R. ELLIOT, *J. Amer. Chem. Soc.*, 67 (1945) 1810.
14 F. C. WHITMORE AND L. H. SOMMER, *J. Amer. Chem. Soc.*, 68 (1946) 481.
15 A. D. PETROV, V. F. MIRONOV AND V. G. GLUKHOVTSEV, *Dokl. Akad. Nauk SSSR*, 110 (1956) 93.
16 L. H. SOMMER AND F. J. EVANS, *J. Amer. Chem. Soc.*, 76 (1954) 1186.
17 L. H. SOMMER, D. L. BAILEY, G. M. GOLDBERG, C. E. BUCK, T. S. BYE, F. J. EVANS AND F. C. WHITMORE
    J. Amer. Chem. Soc., 76 (1954) 1613.
18 A. D. PETROV AND G. I. NIKISHIN, *Zh. obshch. Khim.*, 26 (1956) 1233.
19 W. R. BAMFORD AND B. C. PANT, *J. Chem. Soc. C*, (1967) 1470.
20 R. L. MERKER AND M. J. SCOTT, *J. Amer. Chem. Soc.*, 85 (1963) 2243.
21 H. BOCK, H. SEIDL AND M. FOCHLER, *Chem. Ber.*, 101 (1968) 2815.
22 C. R. HAUSER AND C. R. HANCE, *J. Amer. Chem. Soc.*, 74 (1952) 3091.
23 A. D. PETROV, V. F. MIRONOV AND V. G. GLUKHOVTSEV, *Zh. obshch. Khim.*, 27 (1957) 1535.
24 R. W. BOTT, C. EABORN AND T. W. SWADDLE, *J. Organometal. Chem.*, 5 (1966) 233.
25 H. C. BROWN, J. O. BRADY, M. GRAYSON AND W. H. BONNER, *J. Amer. Chem. Soc.*, 79 (1957) 1897.
26 V. F. MIRONOV AND N. A. POGONIKINA. *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, (1955) 182.