INORG. NUCL. CHEM. LETTERS Vol. 7, pp. 895-899, 1971. Pergamon Press. Printed in Great Britain.

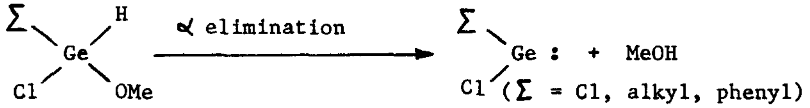
BIVALENT GERMANIUM INTERMEDIATES :
II) INSERTION REACTIONS OF CHLOROGERMYLENES ON TETRAHALIDES OF GROUP IVb ELEMENTS,

M. Massol, J. Barrau and J. Satgé
Laboratoire de chimie des organominéraux - Université Paul Sabatier
Toulouse - France

(Received 18 May 1971)

INTRODUCTION

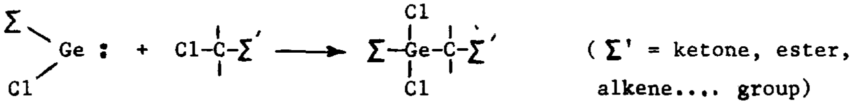
Our previous studies in the field of organomethoxychlorohydrogermanes have demonstrated that these derivatives decompose already at room temperature with formation of divalent germanium species (1) (2) (3).



α elimination

(Σ = Cl, alkyl, phenyl)

After analysis of the behaviour of these germylenes with respect to conjugated dienes (2) (3), organolithium or magnesium compounds (3), we have studied several insertion reactions on halogenated organic derivatives which allow to synthesize new α-or β- functionally substituted germanes (4).

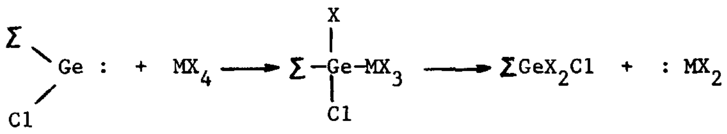


(Σ' = ketone, ester, alkene.... group)

RESULTS

This paper concerns the insertion of the germylenes $\Sigma ClGe:$ (Σ = Cl,Et) on the tetrahalogenated compounds MX_4 of group IVb elements, M = C,Si,Ge,Sn. Owing to the intermediates $\Sigma Cl_2Ge-MCl_3$, these reactions usually lead by exchange to the divalent dihalides MX_2 :

(I)



$$\Sigma ClGe: + MX_4 \longrightarrow \Sigma-GeXCl-MX_3 \longrightarrow \Sigma GeX_2Cl + :MX_2$$

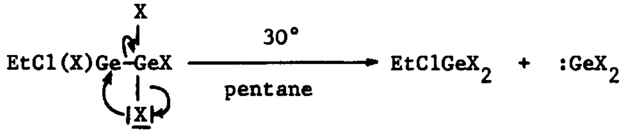
1) Case of germanium : the insertion of ethylchlorogermylene on GeX_4, at normal temperature, yields a limpid, undistillable liquid which has been identified with the digermane $EtClXGeGeX_3$; alkylation at low temperature allows to isolate the stable hexaalkyl digermane :

(II)

$$\begin{tikzcd} \mathrm{EtClGe{:}} + \mathrm{GeX_4} \arrow[r, "20°"] & \mathrm{EtClXGe{-}GeX_3} \arrow[d, "\mathrm{EtMgBr}\ -30°"] \\ & \mathrm{Et_3Ge{-}GeEt_3}(20\ \%) + (\mathrm{Et_2Ge})_n + \mathrm{Et_4Ge} + \mathrm{Et_3GeH} \end{tikzcd}$$

the obtention of Et_4Ge and Et_3GeH corresponds to the decomposition of the digermane by α-elimination with the formation of the most stable tetravalent compound ; in presence of the grignard reagent, the germylene which has been formed leads to polydiethylgermane and Et_3GeH (3)

(III)



$$\mathrm{EtCl(X)Ge{-}GeX} \xrightarrow[\text{pentane}]{30°} \mathrm{EtClGeX_2} + \mathrm{{:}GeX_2}$$

(X = Cl,Br,I)

Such a decomposition has already been reported for mono and dichloro digermanes (5)(6) ; it is quantitative after a long heating (120 hours) at 30-40° and offers an easy approach to the dihalogermylenes in an excellent state of purity. In particular the liquid germanium dichloride, initially obtained with traces of MeOH via the decomposition of $Cl_2Ge(H)OMe$ (4) is here prepared without traces of methanol. The elementary analysis (found % Cl. 48.85 ; calc. 49.41) corresponds to the stoichiometric formula $GeCl_{1.95}$. In a sealed tube at 120° this germanium dichloride disappears quickly and totally in $GeCl_4$. However we can not isolate from the obtained limpid phase, the digermane $Cl_3Ge-GeCl_3$ which has been described in solid form(7). An equilibrium between this digermane and the initial reagents probably takes place, since traces of stable digermane are characterised after alkylation.

(IV)

$$\mathrm{Cl_2Ge{:}} + \mathrm{GeCl_4} \rightleftharpoons [\mathrm{Cl_3Ge{-}GeCl_3}] \xrightarrow[-20°]{\mathrm{EtMgBr}} \underset{\text{(traces)}}{\mathrm{Et_3Ge{-}GeEt_3}} + \mathrm{Et_4Ge} + \mathrm{Et_3GeH} + (\mathrm{Et_2Ge})_n$$

The distillation allows for the recovery of $GeCl_4$; the germanium dichloride remains in form of a white polymer $(GeCl_2)_n$.

2) Case of carbon : the ethylchlorogermylene has been condensed in a sealed tube under thermal effect on carbon tetrachloride. The distillation gives (trichloromethyl) ethyldichlorogermane in a 30 % yield.

(V)

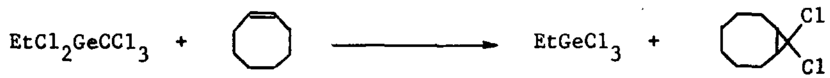
$$\mathrm{EtClGe{:}} + \mathrm{CCl_4} \xrightarrow[4\ \mathrm{j}]{120°} \mathrm{EtCl_2GeCCl_3} + \mathrm{Et_3GeCl} + \text{polymers}$$

($EtCl_2GeCCl_3$: Eb 57-59/0.8 mm ; $n_D^{20} = 1,5089$; $d_4^{20} = 1,6632$; Analysis : found C 12,67 ; H 1,82 ; Cl 60,45 ; $C_3H_5Cl_5Ge$; calc.: C 12,38 ; H 1,73;Cl 60,93 %).

The alkylation with grignard reagent of this derivative is accompanied in this case also, by an α-elimination on the carbon atom, since the tetra-alkylated germanium derivative is isolated at the fractionation :

$$\text{(VI)}\quad EtCl_2GeCCl_3 \xrightarrow[(-20°;\ ether)]{EtMgBr} Et_4Ge \quad (76\ \%\ yield) + polymers$$

Like the (trichloromethyl)-silane (Cl_3SiCCl_3(8)) or-stannane (Me_3SnCCl_3 (9)), the (trichloromethyl)germane is, under thermal effect, a precursor of dichlorocarbene which can be condensed on an olefinic compound. With cyclooctene, the 9,9 dichlorobicyclo (6,1,0) nonane is obtained in a 25 % yield after 14 hours at 200° (yield determined by GLC).

(VII) 

From 120°, in a sealed tube, we observed a sudden and quick dissolution of liquid $GeCl_2$ in the carbon tetrachloride. The limpid colourless phase which had been obtained did not permit to isolate the crystallized (trichloromethyl) trichlorogermane which has already been described (10) (11), owing to a probable equilibrium of the type :

$$\text{(VIII)}\quad Cl_2Ge: + CCl_4 \rightleftharpoons [Cl_3Ge\text{-}CCl_3] \xrightarrow[(-30°)]{EtMgBr} Et_4Ge \quad (60\%\ yield)$$

However, the formation of the trihalomethylated derivative is doubtless, since $GeCl_4$ (65 % yield) is obtained by distillation and the tetraethylgermane by alkylation. The dichlorocarbene which is released under thermal effect can be trapped in an olefinic medium :

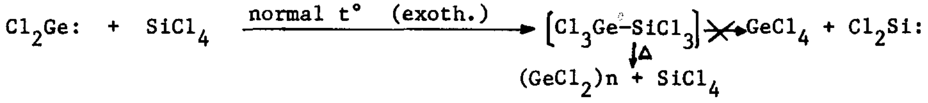
(IX) 

The reaction of ethylchlorogermylene with carbon tetrabromide is slightly exothermic, the formed intermediate derivative $EtClBrGe\text{-}CBr_3$ releases during the distillation the ethylchlorodibromogermane ; several attempts to condense CBr_2 under thermal effect on cyclooctene have failed.

3) Case of silicium : contrary to carbon or germanium tetrahalides which readily insert the germanium divalent compounds, silicium tetrachloride as well as the alkylchlorosilanes R_3SiCl have been inert at 160° in a sealed tube with respect to ethylchlorogermylene. On the other hand, a very exothermic reaction takes place with $GeCl_2$ after mixture of the two reagents and stirring;the transitory formation of a germa-silane $Cl_3GeSiCl_3$ can be

postulated ; however, its decomposition proceeds only by α-elimination on germanium, since only $SiCl_4$ is isolated at the fractionation.

(X)

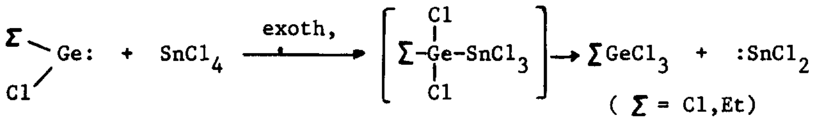


$$Cl_2Ge: + SiCl_4 \xrightarrow{\text{normal t° (exoth.)}} \begin{array}{c}[Cl_3Ge-SiCl_3]\\ \downarrow\Delta \\ (GeCl_2)n + SiCl_4\end{array} \not\rightarrow GeCl_4 + Cl_2Si:$$

The alkylation of the mixture merely yields Et_4Si as definite product and polymers $(Et_2Ge)_n$.

4) <u>Case of tin</u> : the behaviour of the germylenes Cl_2Ge and EtClGe with respect to tin tetrachloride instead is totally different. The reaction, very exothermic, is accompanied by decomposition of the intermediately formed germa-stannane with precipitation of stannous chloride.

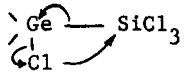
(XI)



$$\begin{matrix}\Sigma\\ Cl\end{matrix}\!\!>Ge: + SnCl_4 \xrightarrow{\text{exoth,}} \left[\begin{array}{c}Cl\\ |\\ \Sigma-Ge-SnCl_3\\ |\\ Cl\end{array}\right] \rightarrow \Sigma GeCl_3 + :SnCl_2 \quad (\Sigma = Cl,Et)$$

The reactivity of the stricly anhydrous pulverulent stannous chloride thus obtained is very different to that of commercial $SnCl_2$ dehydrated by acetic anhydride. The former reacts vigorously with conjugated dienes such as dimethylbutadiene which is immediately polymerized without formation of stannacyclopentene ; with THF this stannous chloride yields a complex $SnCl_2$, THF in a ratio of 1/1 (F° :148-152°)(NMR : signals of the THF protons at $\delta(CH_2O) = 4,42$ ppm and $\delta(CH_2) = 2,08$ ppm), analogs of those described in the literature between $SnCl_2$ and dioxanne or pyridine (12).
It is to be mentioned that the anhydrous commercial $SnCl_2$ does not furnish either of these two reactions under the same conditions. It is probable that, contrary to what happens to the crystallized $SnCl_2$ which is characterized by Sn-Cl-Sn-Cl bond series (12) where tin is at the degree of coordination 6, the $SnCl_2$ prepared in our exchange reactions is associated in a "singulet" state (carbenoid form) more reactive. Lastly, it is to be mentioned that several attempts to obtain the stannylene BuClSn by exchange between Cl_2Ge and $BuSnCl_3$ have given way moreover to the formation of precipitate $SnCl_2$ beside a liquid phase containing $BuSnCl_3$, $GeCl_4$ and also $BuGeCl_3$. The formation of this latter derivative corresponds to a cleavage Sn-C(butyl) which is concurrent with the cleavage Sn-Cl during the α-elimination on the tin atom of the intermediate derivative ($Cl_3Ge-SnCl_2Bu$).

The different insertion-elimination reactions which we have carried out between ΣXGe and MX_4 demand some remarks : in all cases, the insertion leads to an intermediate polyhalogenaled derivative with a Ge-M bond. However, in the case of silicium, the formation of this derivative could not be proved, the α-elimination taking place probably on the germanium only according to :



with an apparent inertness between two reagents such as EtClGe and $SiCl_4$; with $GeCl_2$ the insertion is exothermic, but it ends with a polymerisation of $GeCl_2$. In the case of carbon, if an α-elimination on the Ge is possible and corresponds to the equilibrium (VIII), the disappearance of CCl_2 by condensation on an cycloalkene is likely to displace this equilibrium . In the case of $\Sigma Cl_2Ge-GeCl_3$ and $\Sigma Cl_2Ge-SnCl_3$ (Σ = Et), only the decomposition on the trichlorated group is observed with formation of the most stable tetravalent ΣMCl_3 derivative.

It is difficult to establish a general rule to explain those elimination reactions, especially the particular behaviour of $SiCl_4$ in the MX_4 series with respect to ΣClGe. Nevertheless, these different reactions offer an interest for the obtention of group IVb divalent compounds and we hope to extend them at the preparation of functional carbenes by reaction between Σ ClGe and the derivatives of the Cl_3C-X type (X = functional group).

REFERENCES

(1) M. Massol, J. Satgé, P. Rivière and J. Barrau Communication at the 4th symposium International on organometallic chemistry Bristol (Angleterre). H_3.

(2) M. Massol, P. Rivière, J. Barrau and J. Satgé, C.R. Acad. Sci., 270,(C), (1970), 237.

(3) M. Massol, J. Satgé, P. Rivière and J. Barrau, J. Organometal. Chem, 22, (1970), 599.

(4) M. Massol, J. Barrau, P. Rivière and J. Satgé, J. Organometal. Chem. (sous presse).

(5) E.J. Bulten Thèse Utrecht, 1969.

(6) P. Rivière and J. Satgé, Synth. Inorg. and Metalorg. Chem., 1, (1971), 13.

(7) D. Shriver and W.L. Jolly, J. Amer. Chem. , Soc., 80, (1958), 6692.

(8) W.I. Bevan, R.N. Haszeldine and J.C. Young, Chem. Ind., (London), (1961), 1080.

(9) D. Seyferth and F.M. Armbrecht, J. Amer. Chem. Soc., 91, (1969), 2616.

(10) A. Ponomarenko and G. Ya. Vzenkova, Izvest, Akad. Nauk. SSSR, Ser Khim. Nauk., (1957), 994.

(11) M.J. Mc Glinchey, J.D. Odom, T. Reynoldson and F.G.A. Stone, J. Chem. Soc. (A), (1970), 31.

(12) J.D. Donaldson, Progr. Inorg. Chem., 8, (1967), 403.