Characterisation of Methylpolygermanes

By F. GLOCKLING* and J. R. C. LIGHT
(*Chemistry Department, The University, Durham*)
and J. WALKER
(*Petrochemical and Polymer Laboratories, I.C.I., Runcorn*)

CATENATED ORGANO-DERIVATIVES of the Group IVB elements are of interest in relation to their chemical reactivity and spectroscopic properties.[1,2] Both cyclic $(Me_2Ge)_n$ ($n = 4$ or 6) and non-cyclic methylpolygermanes have been described.[3,4]

We have used two reactions to form methylpolygermanes: (i) GeI_2 + excess Me_3Al in hexane at 20° and (ii) Me_3GeBr + K at 140°. Both yield, by preparative v.p.c., compounds containing up to five germanium atoms together with less volatile compounds, the highest positively identified from its mass spectrum being $Me_{22}Ge_{10}$. In addition, reaction (i) produces minor products resulting from the growth of alkyl chains (*e.g.* Me_9PrGe_4); these are probably formed from $-\!\!\!>\!GeCH_2Al(H)$- intermediates. In reaction (ii) C–H bonds are cleaved, leading to polygermanes of the type $-\!\!\!>\!GeCH_2Ge\!<\!\!\!-$.

The problem of characterising these low-yield

Chemical shifts† *in methylpolygermanes*

Compound	Me_3Ge	Me_2Ge	MeGe	$GeCH_2$	$CH_3(Et)$
Me_4Ge	7·023				
Me_6Ge_2	6·886				
$Me_3GeGe(Me)_2CH_2GeMe_3$	6·945 6·864	6·845		7·123	
$(Me_3Ge)_3GeMe$	6·768		6·691		
$(Me_3Ge)_2Ge(Me)GeMe_2Et$	6·750	6·795	6·709	6·209	6·036
$(Me_3Ge)_4Ge$	6·895				
$(Me_3Ge)_2{}^{a}Ge(Me)Ge(Me)_2GeMe_3{}^{b}$	6·759[a] 6·800[b]	6·677	6·686		

† 1—5% benzene solutions; p.p.m. upfield of benzene.

products (often $<0{\cdot}5\%$) is acute, especially for isomeric compounds. Mass spectrometry establishes molecular formulae and distinguishes between certain isomers (*e.g.* Me_9PrGe_4 and $Me_8Et_2Ge_4$; Me_7EtGe_3 and $Me_3GeCH_2Ge_2Me_5$) by differences in their fragmentation patterns. Unambiguous structural assignments can then be made from their ^1H n.m.r. spectra at 220 Mc./sec., since at this resolution differences in the chemical shifts of Me_3Ge, Me_2Ge, and MeGe protons are sufficient for accurate integration. In general, the methyl resonance moves up-field in the order $Me_3Ge > Me_2Ge > MeGe$, and symmetry factors are apparent in influencing chemical shifts. In a similar way the position of an ethyl or methylene group in a methylpolygermane chain can be determined (see Table).

The reaction between $GeCl_4$ and Me_3GeLi yields the crystalline tetrakis-derivative $(Me_3Ge)_4Ge$, together with $Me_{18}Ge_8$ [probably $(Me_3Ge)_6Ge_2$]. All methylpolygermanes examined are stable in air and are of high thermal stability.

(*Received, June* 18*th*, 1968; *Com.* 803.)

[1] R. West, F. A. Kramer, E. Carberry, M. Kumada, and M. Ishikawa, *J. Organometallic Chem.*, 1967, **8**, 79.
[2] H. Gilman and R. L. Harrell, *J. Organometallic Chem.*, 1967, **9**, 67.
[3] O. M. Nefedov and S. P. Kolesnikov, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1966, 201.
[4] F. Glockling and J. R. C. Light, *J. Chem. Soc.* (*A*), 1967, 623.