Silicon

Poly(diethylsiloxane) liquids. I. Action of sulfuric acid on diethyldiethoxysilane and its mixtures with triethylethoxysilane.

N. S. Leznov, L. A. Sabun and K. A. Andrianov. Zhur. Obshchei Khim. 29, 1270-5 (1959).

It was shown in work done in 1947 that $H_2SO_4$ reacts with $Et_2Si(OEt)_2$ and its mixt. with $Et_2SiOEt$ with the formation of poly(diethylsiloxanes) which are free of polymers contg functional groups. Thus treatment of the polymer, formed by aq. hydrolysis of $Et_2Si(OEt)_2$, with 96% $H_2SO_4$ 1 hr. at 50° gave after aq. washing and neutralization a mixture of poly(diethylsiloxanes) with relatively greater mol. wt. through condensation of the linear polymers at the sites of originally residual EtO groups, as shown by high b.p. range of the polymers and essential absence of EtO groups. A similar effect is produced by contacting the polymers with $HCO_2H$ (70°) or AcOH (90°). Addn. of concd. $H_2SO_4$ to $Et_2Si(OEt)_2$ with cooling gave after stirring the mixt. at 20° to 100° a good yield of poly(diethylsiloxanes), whose mol. wt. and b.t. tended to rise with the rise of temp. of such treatment up to about 75°; at higher temp. the formation of silanol sulfate esters and regeneration of $H_2SO_4$ become predominant and the tendency to form higher polymers declines sharply. In general, elevated temp. tends to favor the formation of polysiloxanes free of linear polymers contg. EtO groups. Heating $Et_2Si(OEt)_2$ and $Et_3SiOEt$ with $H_2SO_4$ 2-3 hrs. at 75° gave linear polymers with HO groups, formed by the aq. treatment of the initially formed sulfate esters. Increased amt. of $Et_3SiOEt$ tends to block the formation of sulfate esters by blocking the HO end-groups of the polymers.

II. Action of phosphoric and boric acids on diethyldiethoxysilane and its mixtures with triethylethoxysilane. Ibid. 1276-81.

Heating $Et_2Si(OEt)_2$ with 3:2 to 1:2 molar proportion of $H_3BO_4$ 1-3 hrs. at 75° gave after an aq. treatment poly(diethylsiloxanes) contg. very little residual EtO groups, the products being 86-8% distillable cyclic polymers. Similar reaction with mixts. of $Et_2Si(OEt)_2$ and $Et_3SiOEt$ gave up to 92%

distillable poly-(diethylsiloxanes). Similar use of $H_3BO_3$ 3-10 hrs. at 95°, finally at 130-40° gave after an aq. treatment 35-54% distillable polysiloxanes with much linear polymer being formed. The reactions yielded as byproducts detectable amounts of $EtOPO_3H_2$ and $(EtO)_3B$. The distn. curves of distillable polysiloxanes formed with the use of $H_3PO_4$ or $H_3BO_3$ were quite similar.

Synthesis of polymers with inorganic molecular chains. I. Poly(organosiloxyphosphoraluminosiloxanes).

K. A. Andrianov, A. A. Zhdanov and L. M. Kazakova. Zhur. Obshchei Khim. 29, 1381-4 (1959). cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959,466. Slow heating of 4.8 g. $(Et_3SiO)_3Al$ with 2.1 g. $Et_3SiOP(O)(OH)_2$ to 200-20° gave a distillate of $(Et_3Si)_2O$ and a residue of a polymer $Et_3SiO[Al(OSiEt_3)OP(O)(OSiEt_3)O]_{14}H$, sol. in MeOH, EtOH and $C_6H_6$. Similar reaction of a 2:1 molar ratio of the reactants 15 hrs. at 220° gave a distillate of $H_2O$ and $(Et_3Si)_2O$ and a residue of viscous liquid polymer $[Et_3SiOAl(OSiEt_3)O]_2P(O)OSiEt_3$. Similarly 4.2 g. $(Et_3SiO)_3Al$ and 4.4 g. $(Et_3SiO)_3PO$ in 21.5 hrs. at 200-20° with a current of moist air drawn through the mixt., gave some $H_2O$ and $(Et_3Si)_2O$, and a residue of transparent yellow resin, sol. in org. solvents and corresponding to $Et_3SiO[Al(OSiEt_3)OP(O)(OSiEt_3)O]_4SiEt_3$. The products pass into infusible insol. solids on being heated further. Similar reactions employing $Me_3SiOP(O)(OH)_2$ or $(Me_3SiO)_3PO$ proceeded very rapidly and directly gave insol. and infusible polymeric products. A kinetic study showed that the viscosity of the new polymers increases with the increasing amt. of distillate formed in the reaction. The starting materials were prepd. as described previously (Voronkov, this j. 25, 469(1955), and Andrianov et al. this j. 28, 267 (1958): $(Et_3SiO)_3PO$, $b_5$ 156-65°, $n_D^{20}$ 1.4462; $(Me_3SiO)_3PO$, $b_4$ 77°, 1.4035; $Et_3SiOP(O)(OH)_2$; $Me_3SiOP(O)(OH)_2$, m. 66.5°.

**Poly-(organometallosiloxanes). 2. Synthesis of poly-(organoalumino-cobaltisiloxanes) and poly-(organoaluminonickelosiloxanes).**

K. A. Andrianov and [illegible]. A. Khdanov (Inst. Hetero-org. Compds., Moscow).

Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1590-4. cf. Doklady Akad. Nauk SSSR 114, 1005 (1957).

Polysiloxanes were synthesized which contain Al and Co or Ni atoms in the polymeric chain. Addn. of 12.99 g. $CoCl_2$ in 117 g. BuOH to 32.24 g. $EtSi(OH)_2ONa$ in 288 g. BuOH at 70° and heating 2.5 hrs. gave after filtration and evapn. a colorless resin which was free of Co. However, the reaction of 32.14 g. $EtSi(OH)_2ONa$, 3.67 g. $AlCl_3$ and 5.25 g. $CoCl_2$ in 400 g. BuOH at 80-100° in 8 hrs. gave after filtration and evapn. 20.13 g. violet polymer, sol. in org. solvents and contg. 23% Si, 7.5% Al and 5.55% Co. Similarly $PhSi(OH)_2ONa$ gave a violet soluble polymer contg. 5.08% Al, 2.8% Co and 16% Si. Similar reaction of $EtSi(OH)_2ONa$ with $AlCl_3$ and $NiCl_2$ in BuOH gave a green polymer, sol. in org. solvents and contg. 6% Al and 1.9% Ni. A series of polymers was prepd. from $EtSi(OH)_2ONa$, $AlCl_3$ and $CoCl_2$ with different proportions of reactants. With increasing ratio of $CoCl_2/AlCl_3$ the polymers have progressively lower content of Al, but the content of Co shows a peak at about 1:1 molar ratio of original salts; this max. peak is about 10% Co in the polymer. The polymer prepd. from $PhSi(OH)_3$ (above) was fractionally pptd.; the richest fraction contained 14.28% Co, 4.4% Al and 15% Si. Removal of the solvent in vacuo from these products resulted in a loss of org. soly.

Poly-(aluminophenylsiloxanes) - infusible but soluble polymers. K. A. Andrianov, A.A.Zhdanov and E.Z.Asnovich (Inst. Hetero-org. Compds. and All Union Electrotechn. Inst., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1760-6. Cf. Doklady Akad. Nauk USSR 102, 85(1955). Addn. of $PhSiCl_3$ to $H_2O$ at 20-5° gave a layer of crude poly-(phenylsiloxane), which ( 25.8 g.) was treated with 8 g. 20% aq. NaOH and heated to 70-5° while 16.63 g. 20% aq. $Al_2(SO_4)_3$ was being added in the presence of an unspecified org. solvent; the mixt. was stirred 2 hrs. at 75° and the sepd. and washed org. layer was evapd. leaving a residue of polymeric product corresponding to repeating units of $C_{24}H_{22}Si_4AlO_{8.5}$. A similar product was obtained by addn. of 40 g. $PhSiCl_3$ to 28.7 g. 20% NaOH and 12.5 g. 10% aq. $Al_2(SO_4)_3$ in the presence of an org. solvent. The product evidently contains 4 Si units per 1 Al unit, with approximately 2 HO groups (on Si atoms) per repeating unit. Fractional pptn. of the product from $CCl_4$ with petr. ether gave fractions ranging in mol. wt. from 5990 to 11800. A similar material was prepd. from $EtSiCl_3$ and corresponded to repeating units $C_{10}H_{27}Si_5AlO_{10}$. The Ph deriv. was sol. in MePh, EtOH, $Me_2CO$ and PhCl. On being heated to 200-500°C, the product became less and less sol. in org. solvents. However the polymer does not melt even at 500°C. Evidently heating converts it to a tridimensional product with extensive crosslinking. The Et deriv. could not be pressed into a mold at 210° as it remained a friable powder. This polymer preserved its org. soly. after being heated to 200° for several hrs. but the soly. is lost rapidly after that period especially at still higher temps. The polymers, prior to being heated, are sol. in many common org. solvents and evidently are constituted on the basis of a complex cyclic struct

Synthesis of organosilicon compds containing the methacrylyl group. K.A.Andrianov and A.K.Dabagova (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1767-71. cf. this j. 1957, 459.

Heating in a rotating autoclave a mixt. of 38.1 g. $ClCH_2SiMe_2OEt$ (I), 45.5 g. $ClCH_2SiMe(OEt)_2$, 45 g. $ClCH_2SiMe_2OBu$, 59.6 g. $ClCH_2SiMe(OBu)_2$ or 74.1 g $ClCH_2Si(OBu)_3$) with 37.2 g. $CH_2:CMeCO_2K$, 5 g. powd. Cu and 0.3 g. hydroquinone 3.5 hrs. at 180° gave the following products: $CH_2:CMeCO_2CH_2SiMe_2OEt$, $b_5$ 72-3°, $d_{20}$ 0.9421, $n_D^{20}$ 1.4300; $CH_2:CMeCO_2CH_2SiMe(OEt)_2$, $b_5$ 97-8°, 0.9753, 1.4260; $CH_2:CMeCO_2CH_2SiMe_2OBu$, $b_5$ 86-7°, 0.9263, 1.4320; $CH_2:CMeCO_2CH_2SiMe(OBu)_2$, $b_5$ 126-7°, 0.9458, 1.4345; $CH_2:CMeCO_2CH_2Si(OBu)_3$, $b_5$ 144-45°, 0.9610, 1.4370. The reaction may be also run at atm. pressure at reflux for 2 hrs., the yields being about 30%. To 12.1 g. I and 4.4 g. $(AcOSiMe_2)_2O$ there was added with cooling 5% by wt. of $EtOSO_3H$ contg. 2% $H_2O$ and the mixt. was kept 2 days; the sepd. org. layer was neutralized with $NaHCO_3$ and distd. yielding 25-33% $CH_2:CMeCO_2CH_2SiMe_2(OSiMe_2)_2CH_2O_2CMe(CH_2$, $b_2$ 147-8°, 0.9862, 1.4390. Similarly were prepd.: $Me_3SiOSiMe(OSiMe_3)CH_2O_2CCMe:CH_2$, $b_2$ 90-1°, 0.9170, 1.4150; $CH_2:CMeCO_2CH_2SiMe_2(OSiMe_2)CH_2O_2CCMe:CH_2$, $b_2$ 162-3°, 0.9953, 1.4360; and $CH_2:CMeCO_2CH_2SiMe_2(OSiMe_2)_2CH_2O_2CCMe:CH_2$, $b_2$ 177-8°, 0.9941, 1.4330. Refluxing 101.5 g. 1,2-dichlorotetramethyldisiloxane or 138.5 g. 1,3-dichlorohexamethyltrisiloxane with 112 g. $Ac_2O$ gave a distillate of AcCl and resp. 1,2-diacetoxytetramethyldisiloxane, $b_{22}$ 94-8°, and 1,3-diacetoxyhexamethyltrisiloxane, $b_{50}$ 140-2 in 60-75% yields. These were: $AcOSiMe_2OSiMe_2OAc$, b. 189°, 1.0232, 1.4010 and $AcOSiMe_2(OSiMe_2)_2OAc$, b. 212°, 1.0131, 1.4030.

**Chloromethylation reaction of arylaliphaticdisiloxanes. Synthesis of chloromethylbenzyldimethylchlorosilane and its derivatives.**

K. A. Andrianov, A. A. Zhdanov and V. A. Odinets. Doklady Akad. Nauk S.S.S. R. 130, 75-8 (1960).

cf. Zhur. Obshchei Khim. 29, 1499 (1959).

Stirring 55.5 g. $PhCH_2SiMe_2Cl$ with 10 g. paraformaldehyde and 100 ml. concd. HCl 4-5 hrs. at 60° while dry HCl was being passed into the mixt. gave an upper layer contg. the chloromethylated material. This crude substance treated with ice and $Et_2O$ gave 60 g. liquid product contg. $(ClCH_2C_6H_4CH_2SiMe_2)_2O$ (I). This (60 g.) and 24 g. $NH_4Cl$ was treated with 60 g. concd. $H_2SO_4$ with ice cooling 15-20 min. and the liq. layer gave on distn. 26 g. $ClCH_2C_6H_4CH_2SiMe_2Cl$, $b_5$ 133°, $d_{20}$ 1.1139, $n_D^{20}$ 1.5234. This with $H_2O$ gave pure I, $b_5$ 232°, 1.0917, 1.5275. When the chloromethylation was attempted in the presence of $ZnCl_2$, the reaction mixt. gave only a viscous undistillable polysiloxane, evidently $(OSiMe_2CH_2C_6H_4CH_2C_6H_4CH_2SiMe_2)_n$. I heated 10 hrs. at 120° with KOAc-AcOH gave $(AcOCH_2C_6H_4CH_2SiMe_2)_2O$, $b_5$ 268-70°, 1.0622, 1.5130, which hydrolyzed with EtOH-KOH in 1 hr. to a product which showed signs of partial reaction or decompn. during attempted distn., leaving a residue of apparently $Me_2Si(OSiMe_2CH_2C_6H_4CH_2OH)_2$.

Silicon

Vinyloxysilanes.

A. N. Nesmeyanov, I. F. Lutsenko and V. A. Bratsev (M.V.Lomonosov State Univ.,Moscow). Doklady Akad.Nauk S.S.S.R. 128, 551-4(1959).

To 32 g. $Hg(CH_2CH)_2$ in 70 ml. isopentane there was added 11 g. $Me_3SiCl$ in 20 ml. isopentane and after refluxing 2 hrs. the filtered mixt. gave 72% $Me_3SiOCH:CH_2$, b. 74-5°, $n_D^{20}$ 1.3835, $d_{20}$ 0.7720. Similarly were prepd. 89% $Et_3SiOCH:CH_2$, $b_{20}$ 53-4°, 1.4275, 0.8505; 77% $ClCH_2SiMe_2OCH:CH_2$, $b_{42}$ 54-5°, 1.4329, 0.9796; 86% $(ClCH_2)_2SiMeOCH:CH_2$, $b_{14}$ 73-3.5°, 1.4646, 1.1515; 64% $Me_2Si(OCH:CH_2)_2$, b. 108.5-9°, 1.4052, 0.8798; 79% $Et_2Si(OCH:CH_2)_2$, $b_{40}$ 69-70°, 1.4246, 0.8890; 82% $MePhSi(OCH:CH_2)_2$, $b_{1.5}$ 65-6°, 1.4940, 0.9959; 81% $ClCH_2SiMe(OCH:CH_2)_2$, $b_{36}$ 72.5-3°, 1.4386, 1.0457; 71% $MeSi(OCH:CH_2)_3$, $b_{30}$ 50-1°, 1.4133, 0.9457; 76% $EtSi(OCH:CH_2)_3$, $b_{40}$ 69-70°, 1.4225, 0.9503; 70% $PhSi(OCH:CH_2)_3$, $b_2$ 79-80°, 1.4896, 1.0385; 72% $Si(OCH:CH_2)_4$, $b_{12}$ 53-3°, 1.4146, 0.9949. To 125 g. $ClHgCH_2Ac$ in $C_6H_6$ there was added 32 g. pyridine and 17 g. $SiCl_4$ in $C_6H_6$; after 1.5 hrs. refluxing the filtered mixt. gave 49% $Si(OCMe:CH_2)_4$, $b_5$ 76°, 1.4320, 0.9722. Similarly were obtained: 58% $Et_3SiOCMe:CH_2$, $b_{20}$ 65-6°, 1.4290, 1.8365(???); 63% $Et_3SiOCEt:CHMe$, $b_3$ 55-6°, 1.4432, 0.8497; 45% $Et_3SiOCPh:CH_2$, $b_3$ 106-7°, 1.5089, 0.9466; 87% $(EtO)_3SiOCH:CH_2$, $b_{30}$ 76-7°, 1.3905, 0.9493.

Silicon

Reactivity of α-, β- and γ-chloroalkylsilane chlorides in the Friedel-Crafts reaction.

B. A. Chernyshev and M. E. Dolgaya (Inst. Org. Chem., Acad. Sci., Moscow).

Zhur. Obshchei Khim. 29, 1850-3 (1959). cf. 28, 2829(1958).

Detn. of the rates of HCl evolution in a Friedel-Crafts reaction of various chloroalkylsilane chlorides and $C_6H_6$ gave the following reaction rate constants at 30°: $Cl_3SiCH_2Cl$ $2.36X10^{-4}$ mole/min.; $Cl_3SiCH_2CH_2Cl$ $4.28X10^{-3}$; $Cl_3Si(CH_2)_3Cl$ $5.48X10^{-3}$; $MeSiCl_2CH_2Cl$ $3.67X10^{-4}$; $MeSiCl_2(CH_2)_2Cl$ $4.47X10^{-2}$; $EtSiCl_2(CH_2)_2Cl$ $4.17X10^{-2}$; $MeSiCl_2(CH_2)_3Cl$ $6.72X10^{-3}$; $Cl_3SiCHMeCl$ $2.39X10^{-4}$; $EtSiCl_2CHMeCl$ $2.96X10^{-4}$. Reaction of $Cl_3Si(CH_2)_2Cl$ with PhCl had the rate constant of $1.67X10^{-3}$ and with MePh $5.95X10^{-3}$.

Silicon

Synthesis and transformations of unsaturated organosilicon compounds. II. Synthesis of silicohydrocarbons of vinylacetylene series.

I. A. Shikhiev, M. F. Shostakovskii and L. A. Kayutenko ( Inst. Org.Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 2137-9 (1959). cf. Doklady Akad. Nauk SSSR 109, 344(1956).

Heating 15 g. bis-(1,1-dimethyl-2-propyne-1-ol)-ethylsilane with 13.6 g. $TlSO_4$ in the presence of hydroquinone to 65° gave after distn. an unstated yield of $(CH_2:CMeC{\equiv}C)_2SiHEt$, $b_4$ 76-7°, $n_D^{20}$ 1.5010, $d_{20}$ 0.8518. Similarly were prepd.: $(CH_2:CMeC{\equiv}C)_2SiMe_2$, $b_4$ 75-5.5°, 1.5000, 0.8475; $(CH_2:CMeC{\equiv}C)_2SiEt_2$, $b_6$ 105°, 1.5027, 0.8594; $(CH_2:CMeC{\equiv}C)_2SiMeEt$, $b_2$ 87-8°, 1.5000, 0.8583; $(CH_2:CMeC{\equiv}C)_2SiMePr$, $b_{10}$ 113°, 1.4990, 0.8555. These hydrogenated to the satd. analogs over Raney Ni in MeOH.

silicon

Organomagnesium synthesis of α- and β-trimethylsilylacrylic acids and vinyl derivatives of silicon, germanium and tin.

V. F. Mironov, A. D. Petrov and N. G. Maksimova (N.D.Zelinskii Inst.Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1954-60.

The Normant method was used to prepare the following substances. RMgX from 11 g. Mg and 50 g. $CH_2$:CHBr, activated by a little PrBr, in tetrahydrofuran, was treated with $Et_3SnCl$, yielding 60% $Et_3SnCH$:$CH_2$, b. 174-5°, $n_D^{20}$ 1.4780, $d_{20}$ 1.2133. Similarly was prepd. 55% $Et_2Ge(CH:CH_2)_2$, $b_{745}$ 149.8°, 1.4575, 1.0193; 32% $EtSiH(CH:CH_2)_2$, b. 93-4.3°, 1.4305, 0.7554; $Et_2Si(CH:CH_2)_2$, $b_{746}$ 138.3°, 1.4435, 0.7911; $MePhSi(CH:CH_2)_2$, $b_{11}$ 93.5-4.5°, 1.5185, 0.9069; $MeEtSi(CH:CH_2)_2$, $b_{745}$ 111°, 1.4295, 0.7623; $MeSi(CH:CH_2)_3$, $b_{747}$ 101.9°, 1.4405, 0.7692; $EtSi(CH:CH_2)_3$, $b_{744.5}$ 133.6°, 1.4525, 0.7930; $Et_2Sn(CH:CH_2)_2$, $b_{765}$ 168.5°, 1.4860, 1.2356. Addn. of $Br_2$ to $MeSiCl_2CH$:$CH_2$ under incandescent lamp with cooling gave 94% $MeSiCl_2CHBrCH_2Br$, $b_4$ 101°, 1.5335, 1.9221. Similarly was prepd. 90% $EtSiCl_2CHBrCH_2Br$, $b_{739}$ 240°, $b_7$ 142°, 1.5320, 1.8227. Distn. of $BrCH_2CHBrSiCl_3$ from quinoline or $PhNEt_2$ gave 65% $CH_2$:$CBrSiCl_3$, $b_{749}$ 145.5°, 1.4928, 1.7151. Similarly was prepd. 58% $CH_2$:$CBrSiMeCl_2$, $b_{735}$ 145-3.5°, 1.4870, 1.5594, and $CH_2$:$CBrSiEtCl_2$, 40%, $b_{20}$ 135°, 1.4370, 1.4458. MeMgI and $CH_2$:$CBrSiCl_3$ gave 74% $CH_2$:$CBrSiMe_3$, $b_{41}$ 47-8°, $b_{745}$ 124°, 1.4580, 1.1562 (Raman spectrum shown). EtMgBr similarly gave 30% $Et_3SiCBr$:$CH_2$, $b_{25}$ 92°, 1.4770, 1.1273. Heating 573 g. $BrCH_2CH_2SiCl_3$ with 1 g. $AlCl_3$ gave 28.7% BrCH:$CHSiCl_3$, b. 155-6°, 1.5030, 1.7207. This with MeMgCl gave 42% $BrCH:CHSiMe_3$, $b_{42}$ 55°, 1.4675, 1.1628 (Raman spectrum shown). This with Mg in tetrahydrofuran gave the RMgBr which with $Me_3SiCl$ gave only $Me_3SiCH:CHSiMe_3$. Carbonation of the above RMgBr gave 64% $Me_3SiC(:CH_2)CO_2H$, $b_{13}$ 97-105°, m. 50°. Similarly was prepd. 46% $Me_3SiCH:CHCO_2H$, $b_{13}$ 113°, $n_D^{25}$ 1.4500, m. 25-5.5°.

silicon

Reaction of tetraalkyldihydrosilanes with difunctional unsaturated compounds.

V. V. Korshak, A. M. Polyakova, V. M. Vdovin, V. F. Mironov and A. D. Petrov (Inst. Hetero-org. Compds., Moscow). Doklady Akad. Nauk S.S.S.R. 128, 960-3 (1959). cf. Izvest. Akad. Nauk SSSR, otd.kh.nauk, 1929, No.12, no pp given. It was shown that dihydrosiloxanes add to organometallic compds. with 2 unsatd. radicals and yield polymeric products. Unsatd. Si and Ge compds. react satisfactorily, while those of Sn do not react and those of Pb undergo a decompn. with loss of Pb. Treatment of $MeSiHCl_2$ with EtMgCl gave 67% MeEtSiHCl, b. 85-96°, which treated with $H_2O$-$Et_2O$ gave 88.5% $O(SiHMeEt)_2$, b. 125.5-6°, $n_D^{20}$ 1.3980, $d_{20}$ 0.7935. Similarly was prepd. 88% ~~O(SiHEt)2~~ $Et_2SiHCl$, b. 98.5-101.5°, $n_D^{20}$ 1.4154, which gave 75-93% $O(SiHEt_2)_2$, b. 172-3°, 1.4160, 0.8159. EtMgBr and $EtSiHCl_2$ gave $Et_3SiH$ and $O(SiHEt_2)$ after an aq. treatment. Similarly was prepd. $O(SiMe_2H)_2$, b. 70-1°, 1.3700, 0.7572. The dihydrosilanes above were shaken in sealed ampuls with: $Et_2Si(CH{:}CH_2)_2$, $PhMeSi(CH{:}CH_2)_2$, $Et_2Ge(CH{:}CH_2)_2$, $Me_2Ge(CH_2CH{:}CH_2)_2$, $Et_2Si(CH_2CH{:}CH_2)_2$, $Me_2Si(OCH_2CH{:}CH_2)_2$, $Et_2Si(OCH_2CH{:}CH_2)_2$ or $Me_2Si(CH_2CH{:}CH_2)_2$, in the presence of 0.01 g. per 0.12 mole of $H_2PtCl_6$ catalyst; the reactions were then completed by 6 hrs. at 120°. All the listed monomer combinations yielded appropriate polymeric products, the analyses of which are reported.

**Synthesis of α,ω-bis-(cyanoalkyl)-tetra-alkyldisiloxanes.**

A. D. Petrov, V. M. Vdovin and R. Sultanov (N.D.Zelinskii Inst. Org. Chem., Moscow), Doklady Akad. Nauk S.S.S.R. 128, 1204-7 (1959). cf. this j. 100, 711 (1955).

Stirring 19.3 g. $NC(CH_2)_3SiMeEtCl$ with 25 ml. $H_2O$ 5 hrs. gave after extn. with $Et_2O$ 10.3 g. $(NC(CH_2)_3SiMeEt)_2O$, $b_3$ 195-7°, $b_3$ 193° (redistd.), $n_D^{20}$ 1.4513, $d_{20}$ 0.9377. This was also formed from $NC(CH_2)_3SiEtCl_2$ and MeMgCl, followed by treatment with $H_2O$. Similarly were prepd.: $NC(CH_2)_3SiEtCl_2$, $b_3$ 99°, 1.4625, 1.1295; $NC(CH_2)_3SiMeEtCl$, $b_4$ 121°, 1.4515, 0.9895; $NC(CH_2)_3SiEtMe_2$, $b_3$ 66°, 1.4363, 0.8377; $NC(CH_2)_2O(CH_2)_3SiMeEtCl$ (I), $b_1$ 123°, 1.4555, 1.0098; $(NCCH_2CH_2SiEt_2)_2O$, $b_2$ 175°, 1.4605, 0.9470; $(NCCH_2CH_2CH_2SiMe_2)_2O$, $b_2$ 161-2°, 1.4441, 0.9344; $(NCCH_2CH_2CH_2SiEt_2)_2O$, $b_{1.5}$ 193°, 1.4593, 0.9413; $(NCCH_2CH_2OCH_2CH_2CH_2SiMeEt)_2O$, undistillable, 1.4552, 0.9741. Stirring I with concd. HCl finally at 80-90° gave $(HO_2CCH_2CH_2OCH_2CH_2CH_2SiMeEt)_2O$, an oil. To 160 g. NCCH:$CH_2$, 90 g. $PhNEt_2$ mixt. there was added over 8 hrs. 410 g. $HSiCl_3$ at reflux, and after 32 hrs. further refluxing there was obtained some $Cl_3SiCH_2CH_2CN$, $b_{15}$ 96-8°, m. 26-30°, sepd. from $PhNEt_2$ by freezing-out.

**Addition of hydrosilanes to dimethylvinylethynylcarbinol and the product of its cyanoethylation.**

A. D. Petrov and S. I. Sadykh-Zade (N.D.Zelinskii Inst. Org. Chem., Moscow). Doklady Akdd. Nauk S.S.S.R. 129, 584-7 (1959). cf. this j. 112,662(1957). Addn. of 53 g. $Et_3SiH$ to 55 g. $CH_2:CHC:CCMe_2OH$ and 0.5 ml. 0.1 N $H_2PtCl_6$ and heating the mixt. to 170° gave 62% $CH_2:CHC(SiEt_3):CHCMe_2OH$, (I) $b_1$ 85-5.5°, $n_D^{20}$ 1.4861, $d_{20}$ 0.8873. Similarly $NCCH_2CH_2OCMe_2C:CCH:CH_2$ and $EtSiHCl_2$ reacted in iso-PrOH in the presence of $H_2PtCl_6$ at 90° ( very exothermic) and gave 61% $NCCH_2CH_2OCMe_2CH:C(SiEtCl_2)CH:CH_2$, $b_3$ 150-1°, 1.4865, 1.0846. Similarly was prepd. $CH_2:CHC(SiEt_3):CHCMe_2OCH_2CH_2CN$, 75%, $b_3$ 158°, 1.4840, 0.9196; 54% $CH_2:CHC(SiMeCl_2):CHCMe_2OCH_2CH_2CN$, $b_4$ 146-8°; 90% 2-methyl-4-(triethylsilyl)-1,3,5-hexatriene, $b_3$ 91°, 1.4920, 0.8759, was obtained by treating I with $KHSO_4$.

Silicon

**Addition of trichlorosilane to dialkyl(phenyl, chloro)-diallylsilanes in the presence of $H_2PtCl_6.6H_2O$.**

A. V. Topchiev, N. S. Nametkin and S. G. Durgar'yan. Doklady Akad. Nauk S.S.S.R. 130, 105-8 (1960). cf. Sommer et al. JACS 69, 188(1947).

The following silanes were prepd. by addn. of $HSiCl_3$ to various diallylsilanes in the presence of 1 ml. catalyst composed of M soln. of $H_2PtCl_6.6H_2O$ in iso-PrOH with heating 10 hrs. at 50° and 2 hrs. at 80°: 28.5% $CH_2:CHCH_2SiMe_2CH_2CH_2CH_2SiCl_3$, $b_7$ 115-8°; 29% $CH_2:CHCH_2SiEt_2(CH_2)_3SiCl_3$, $b_4$ 124-6°; 29.7% $CH_2:CHCH_2SiPr_2(CH_2)_3SiCl_3$, $b_9$ 167-9°; 28.8% $CH_2:CHCH_2SiBu_2(CH_2)_3SiCl_3$, $b_9$ 186-9°; 17.6% $CH_2:CHCH_2SiPh_2(CH_2)_3SiCl_3$, $b_4$ 222-4°; 13.8% $CH_2:CHCH_2SiMePh(CH_2)_3SiCl_3$, $b_5$ 180-2°; 8.3% $CH_2:CHCH_2SiCl_2(CH_2)_3SiCl_3$, $b_4$ 153-6°; $Me_2Si(CH_2CH_2CH_2SiCl_3)_2$, 27.9%, $b_{.55}$ 163-5°; 32% $Et_2Si(CH_2CH_2CH_2SiCl_3)_2$, $b_5$ 176-8°; 32.6% di-Pr analog, $b_5$ 193-5°; 34% di-Bu analog, $b_5$ 219-21°; 52.4% di-Ph analog, $b_4$ 268-70°; 41.4% $MePhSi(CH_2CH_2CH_2SiCl_3)_2$, $b_5$ 213-4°; 67.3% $Cl_2Si(CH_2CH_2CH_2SiCl_3)_2$, $b_2$ 210-2°.

Synthesis of organosilicon monomers from methylchlorosilane.

V. A. Ponomarenko, G. V. Odabashyan and A. D. Petrov (N.D.Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 130, 333-5 (1960). cf. 126, 1009 (1959).

Slow distn. through a column of 200 g. $MeSiHCl_2$ and 14 g. activated dimethylcyanamide gave $MeSiH_2Cl$, $b_{745}$ 8-9°, which was added to appropriate unsatd. compds/ conventionally in the presence of $H_2PtCl_6$. $EtSiH_2Cl$ was employed similarly. The following products are listed: MeEtSiHCl, $MeEt_2SiCl$, MePrSiHCl, $Me(CF_3CH_2CH_2)SiHCl$, $Me(CF_3CH_2CH_2)_2SiCl$, $MeEtSiClCH_2CH_2CF_3$, $MeEtSiClCH_2CH_2SiClMeEt$ and $MePhSiClCH_2CH_2SiClMePh$. The yields were 18-69%. Passage of $MeSiHCl_2$ and PhCl through a hot tube at 635-45° gave a range of products from which was isolated 15.5% MePhSiHCl, $b_{740}$ 176°, $d_{20}$ 1.0540, $n_D^{20}$ 1.5171. This was similarly added to various unsatd. compds. Passage of $MeSiH_2Cl$ and $CH_2$:CHCl through a tube at 550-600° gave 11.5% $Me(CH_2:CH)SiHCl$, $b_{761}$ 60.5°, 0.9125, 1.4140. Also listed are: MePhSiHCl, $b_{740}$ 176°, 1.0540, 1.5171; $MePhSiCl_2$, $b_{740}$ 197°, 1.1814, 1.5194; $Me(CF_3CH_2CH_2)SiHCl$, $b_{746}$ 96.5°, 1.1565, 1.3651; $Me(CF_3CH_2CH_2)_2SiCl$, $b_6$ 45.5-7°, 1.2791, 1.3699; MeEtSi-$(CH_2CH_2CF_3)Cl$, $b_{758}$ 140°, 1.1044, 1.3871; $MeEtSiClCH_2CH_2SiClMeEt$, $b_{10}$ 100.5-1.5°, 0.9981, 1.4580; $MePhClSiCH_2CH_2SiClMePh$, $b_9$ 207-9°, m. 59-60°.

Reaction of tetra-alkyldihydrodisiloxanes with difunctional unsaturated compounds.

[illegible] Tolvakova and N. A. Chumaevskii. Doklady Akad. Nauk S.S.S.R. 130, 1037-40 (1960).

Infra-red spectra are shown for the reaction products of $(R_2SiH)_2O$ with unsatd. difunctional compds. centered on Si or Ge atoms and contg. 2 vinyl groups (cf. this j. 128, 900(1959) for the prepn.). Spectra are also shown for the following monomers: $(Me_2SiH)_2O$, $(MeEtSiH)_2O$, $(Et_2SiH)_2O$, $MePhSi(CH:CH_2)_2$, $Et_2Si(CH:CH_2)_2$, $Et_2Si(CH:CH_2)_2$ and $CH_2:CHCH_2CH_2CH:CH_2$. The polymeric products from ~~xxix~~ the selected monomer pairs fail to show any residual Si-H frequencies in their spectra, after reppt. from EtOH. The Si-H bond frequency does appear in spectra of products formed from excess disiloxane component reacting with the divinyl deriv. as it does in the polymer formed from the reaction with 2,5-hexadiene. Diallylic derivs. tend to produce products with residual vinyl or C:C bonding. It is suggested that the divinyl monomers reacting with equimolar amounts of the disiloxanes yield products which are probably cyclic in nature, while the diallylic monomers tend to yield linear products.

Silicon

Organic compounds of boron.

B. M. Mikhailov. Uspekhi Khim. 28, 1450-87 (1959).

A review covering the synthesis and the general properties of organoboron compds, with 176 references through 1958.

Organoboron

Organoboron compounds. XXXIV. Alkylphenylboron chlorides.

B. M. Mikhailov and P. M. Aronovich (Inst. Org. Chem., Acad. Sci., Moscow).

Zhur. Obshchei Khim. 29, 1254-7 (1959). cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 546.

Treatment of 127 ml. (iso-BuO)$_2$BPh in $Et_2O$ at -70° over 3-4 hrs. with MeMgBr from 13.4 g. Mg, stirring 4-5 hrs. and setting the mixt. aside at -70° overnight gave after treatment with aq. HCl 71% iso-BuOBMePh, $b_7$ 88-9°, $n_D^{20}$ 1.4862, $d_{20}$ 0.8940. Similar reaction with EtLi gave 68.5% iso-BuOBEtPh, $b_6$ 95-6°, 1.4828, 0.8923, which on prolonged heating to 100° undergoes disproportionation. Shaking iso-BuOBRPh with 36% HCl resulted in a homogeneous soln. in 1-2 days which yielded ROH on distn. along with some unreacted ester. Treatment of 0.2 mole iso-BuOBRPh with 37.5 g. $PCl_5$ at 60-70° 10-15 min. gave: 81% PhMeBCl, $b_{24}$ 68-9°, $d_{20}$ 1.0440; 83.3% PhEtBCl, $b_{20}$ 85-6°, 1.0328; 76.4% PhPrBCl, $b_9$ 83-4°, 1.0274; 82.5% PhBuBCl, $b_7$ 90-1°, 0.9966.

Organoboron compounds. XXXV. Alkylphenylboronic acids and their anhydrides. B. M. Mikhailov and P. M. Aronovich (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 1257-62 (1959). cf. 29, 1254 (1959).

Addn. of 0.1 mole PhRBCl in 1 vol. $Et_2O$ to 16.5 ml. 20% NaOH with ice cooling, shaking and extn. of the aq. layer with $Et_2O$, gave after washing the combined org. layers with $H_2O$, drying and evapg. in vacuo the following liquid and very easily oxidizable PhRBOH: (R shown) Me, 85%, $n_D^{20}$ 1.5202, $d_{20}$ 0.9729; Et, 78.5%, 1.5102 (at 24°), 0.9514 (at 24°); Pr, 82.4%, 1.5030, 0.9429; Bu, 90%, 1.4987, 0.950. Distn. of these in vacuo gave $(PhRB)_2O$: Me, $b_8$ 137-8°, 1.5440, 0.9666; Et, $b_3$ 130-2°, 1.5419 (at 24°), 0.9526 (at 24°); Pr, $b_5$ 156-8°, 1.5343, 0.9575; the Bu member gave a range of products with $b_{0.3}$ 110-65° and left a residue of phenylboronic anhydride. Shaking 1 g. $(PhEtB)_2O$ with 3 ml. $Et_2O$ and 1 ml. $H_2O$ 1 hr. gave on evapn. of the org. layer a liquid residue of PhEtBOH, $n_D^{24}$ 1.5130. If the hydrolysis is run with 20% NaOH, the aq. layer yields 96% $PhEtB(OH)_2Na$, needles (from $Me_2CO$) which are very hygroscopic. Similarly was prepd. 89% $PhPrB(OH)_2Na$, needles. MePhBCl and $H_2O$-$Et_2O$ mixed with icecooling gave after evapn. a mixture of methylboronic and methylphenylboronic acids. PhEtBCl similarly gave mainly ethylboronic acid, while PhPrBCl gave mixed propylphenylboronic and propylboronic acids. PhBuBCl gave some butylboronic acid. Keeping PhEtBOH in concd. HCl-$Et_2O$ (exothermic reaction on mixing) gave after 1 day some $C_6H_6$ and ethylboronic acid; the same ester kept in $Et_2O$-HCl 3 days showed no change. Evidently hydrolysis of PhRBCl is accomplished through initial complex formation of $H_2O$ at the B atom, followed by loss of $C_6H_6$.

**Organoboron compounds. XXXVI. Synthesis of hexa-substituted borazole from esters of arylchloroboronic acids.**

B. M. Mikhailov and T. V. Kostroma (Inst. Org. Chem., Acad. Sci., Moscow)
Zhur. Obshchei Khim. 9, 1477-83 (1959). cf. Izvest.Akad.Nauk SSSR 1957, 1125.

Heating esters of arylethylaminoboronic acids to 300° converts them to borazoles and esters of arylboronic acids. To 14.3 g. o-$MeC_6H_4BClOCH_2CHMe_2$ in 20 ml. $Et_2O$ there was added at -30° 8.75 ml. $EtNH_2$ in $Et_2O$ and after 0.5 hr. at -30° and 1 hr. at room temp., the mixt. was filtered and rapidly distd. yielding 84% o-$MeC_6H_4B(OCH_2CHMe_2)NHEt$, $b_3$ 93-5°, $n_D^{20}$ 1.4847, $d_{20}$ 0.9042. This heated to 260° does not form a borazole, being different in this respect from the other esters below. Similarly was prepd. 59.4% p-$MeC_6H_4B(OCH_2CHMe_2)NHEt$, (I) $b_2$ 110-12°, 1.4891, 0.9059; 52.4% 1-$C_{10}H_7B(OCH_2CHMe_2)NHEt$, $b_9$ 188-5°, 1.5470, 0.9750. I (9.8 g.) heated 1 hr. at 260°, cooled and extd. with isopentane gave a ppt. of 1.2 g. B,B,B-tri-p-tolyl-N,N,N-triethylborazole, m. 228-5°. The filtrate gave 5.64 g. mixed starting ester and p-$MeC_6H_4B(OCH_2CHMe_2)_2$. To 19.65 g. $PhBClOCH_2CHMe_2$ in 20 ml. $Et_2O$ there was added 18.62 g. $PhNH_2$ in $Et_2O$ and stirred 1 hr.; after filtration there was isolated 7.5 g. $PhB(OCH_2CHMe_2)_2$, $b_{21}$ 146-50°, some $PhNH_2$, and 30% hexaphenylborazole, m. 380-5°, isolated after distn. of the above ester. Similarly p-$MeC_6H_4BClOCH_2CHMe_2$ and $PhNH_2$ gave p-$MeC_6H_4B(OCH_2CHMe_2)_2$, $b_{10}$ 145-50° and 39% B,B,B-tri-p-tolyl-N,N,N-triphenylborazole, m. 282-4° (from $C_6H_6$-isopentane). Heating 2.1 g. $PhB(NHEt)_2$ with 0.2 ml. iso-BuOH 2 hrs. at 270° gave $EtNH_2$ and 85.2% B,B,B-triphenyl-N,N,N-triethylborazole, m. 205-9°. Treatment of 19.6 g. $PhBClOCH_2CHMe_2$ in $Et_2O$ with 18.62 g. $PhNH_2$ 1 hr., filtration and high vacuum distn. gave 76.9% $PhB(OCH_2CHMe_2)_2$ and 79.4% $PhB(NHPh)_2$, $b_{0.06}$ 178-80°, m. 84-6°. Similarly p-$MeC_6H_4BClOCH_2CHMe_2$ gave 85.9% p-$MeC_6H_4B(OCH_2CHMe_2)_2$ and 83.6% p-$MeC_6H_4B(NHPh)_2$, $b_{0.04}$ 163-5°, m. 100-2°. The latter distd. at ca. 400° gave $PhNH_2$ and 33.8% B,B,B-tri-p-tolyl-N,N,N-triphenylborazole, m. 282-4°.

Organoboron compounds. XXXVII. Synthesis of B-triarylborazoles from arylboron dichlorides.

B. M. Mikhailov, A. N. Blokhina and T. V. Kostroma (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 1483-6 (1959). cf. prec. abstr.

The following reactions were run under $N_2$. To 70 g. $PhB(OBu)_2$ there was added 62 g. $PCl_5$ so as to maintain the temp. at 70-80° with water cooling and after the reaction had subsided the remaining 62 g. $PCl_5$ was added at once and the mixt. stirred 1 hr. on a steam bath. Distn. gave 60% $PhBCl_2$, $b_{37}$ 87-9°. Similarly $p\text{-}MeC_6H_4B(OCH_2CHMe_2)_2$ gave 50% $p\text{-}MeC_6H_4BCl_2$, $b_7$ 91-4°, m. 25-7°. Similarly was prepd. 66.3% $p\text{-}BrC_6H_4BCl_2$, $b_{20}$ 114-4.5°, m. 36-8°. Passage of $NH_3$ 0.5 hr. into 4.3 g. $p\text{-}MeC_6H_4BCl_2$ in 50 ml. $C_6H_6$, was followed by addn. of $NH_3$ over 1 hr. on a steam bath; the mixt. was centrifuged, evapd. and treated with isopentane yielding 64.3% B,B,B-tri-p-tolylborazole, m. 189-90° (from $C_6H_6$-isopentane). Similarly was prepd. 66.5% B,B,B-tri-p-bromophenylborazole, m. 292-3°, and 91.3% B,B,B-tri-p-chlorophenylborazole, m. 269-70°. Treatment of 2.7 g. $PhBCl_2$ in $Et_2O$ at -10° with $Et_3N$ gave a ppt. of $PhBCl_2 \cdot Et_3N$, m. 80-4°.

**Organoboron compounds. XXXVI. Unsymmetric diarylboronic acids and their derivatives.**

B. M. Mikhailov and N. S. Fedotov (Inst. Org. Chem., Acad. Sci., Moscow).
Zhur. Obshchei Khim. 29, 2244-8 (1959). cf. Izvest.Akad.Nauk SSSR, Otdel. Khim. Nauk 1958, 419.

All reactions below were run under $N_2$. Reaction of 0.4 mole $1\text{-}C_{10}H_7MgBr$ and 88.3 g. $PhB(OCH_2CHMe_2)_2$ in $Et_2O$ at -60° gave after treatment with dil. HCl 80% $1\text{-}C_{10}H_7BPhOCH_2CHMe_2$ (A), $b_8$ 207-8°, $d_{20}$ 1.099, $n_D^{20}$ 1.597; passage of $NH_3$ in $Et_2O$ soln. of this gave the $NH_3$ adduct, m. 90-2° (in sealed tube). Similarly was prepd. 41% $(p\text{-}MeC_6H_4)BPhOCH_2CHMe_2$ (I), $b_{1.5}$ 126-8°, 0.9720, 1.5552; $NH_3$ adduct, m. 87-9°. Treatment of I with 100% excess $H_2NCH_2CH_2OH$ gave 87.3% $(p\text{-}MeC_6H_4)BPhOCH_2CH_2NH_2$, m. 163-5°. $PhB(OCH_2CHMe_2)_2$ and $p\text{-}BrC_6H_4MgBr$ gave 33% $(p\text{-}BrC_6H_4)BPhOCH_2CHMe_2$, $b_2$ 152-3°, 1.9199, 1.5773. Treatment of 13 g. A with 9.4 g. $PCl_5$ with heating to 50-60° gave 76.3% $1\text{-}C_{10}H_7BPhCl$ (II), $b_4$ 180-1°, m. 87-90°. Similarly was prepd. 50% $p\text{-}MeC_6H_4BPhCl$, $b_8$ 142-4°, $d_{20}$ 1.5783.

Treating I in $Et_2O$ with N NaOH with ice cooling gave after evapn. and treatment with isopentane at -40° a low yield of $1\text{-}C_{10}H_7BPhOH$, m. 57-9°. Similarly was prepd. $p\text{-}MeC_6H_4BPhOH$, an oil, which on standing transformed into 88% $(PhBO)_3$, m. 212-4°. $p\text{-}MeC_6H_4BPhCl$ forms an equimolar adduct with dioxane, m. 72-6°. Similar adduct formed with $Ph_2BCl$, m. 80-5°, and with $(1\text{-}C_{10}H_7)_2BCl$, m. 93-6°, and with $1\text{-}C_{10}H_7BPhCl$, m. 90-1°. These are not stable in storage.

Organoboron compounds. XXXVII. Lithium salts of diarylboronic acids and their complex compounds with dioxane.

B. M. Mikhailov and V. A. Vaver (Inst. Org. Chem., Acad. Sci., Moscow).

Zhur. Obshchei Khim. 29, 2248-53 (1959). cf. preced.abstr.

Diarylboronic acids react like protonic acids in nonaqueous media. All the reactions below were run under $N_2$. Addn. of 0.018 mole BuLi soln. to 5 g. $(1\text{-}C_{10}H_7)_2BOH$ in dry $C_6H_6$ gave in 10 hrs. a crystn. ppt. of its Li salt. Similarly $(p\text{-}MeC_6H_4)_2BOH$ and $p\text{-}MeC_6H_4Li$ gave the Li of the former acid, a crystn. solid. (I) $(o\text{-}MeC_6H_4)_2BOH$ with BuLi in hexane-$C_6H_6$ gave a ppt. of mixed $(o\text{-}MeC_6H_4)_2BBuOH.Li$ and its cleavage products $(o\text{-}MeC_6H_4)_2BLi$ and $(o\text{-}MeC_6H_4)BBuOLi$. This mixt. treated with dioxane in $Et_2O$ gave on evapn. of the org. layer and treatment with isopentane in the cold a ppt. of $(o\text{-}MeC_6H_4)_2BOLi.O(CH_2CH_2)_2O$, which also formed from $(o\text{-}MeC_6H_4)_2BOH$ and $o\text{-}MeC_6H_4Li.O(CH_2CH_2)_2O$. The latter procedure also gave from $p\text{-}MeC_6H_4Li.O(CH_2CH_2)_2O$ and $(p\text{-}MeC_6H_4)_2BOH$ in $Et_2O$-dioxane a ppt. of relatively insol. $(p\text{-}MeC_6H_4)_2BOLi.O(CH_2CH_2)_2O$, while the filtrate gave $(p\text{-}MeC_6H_4)_3BOH.Li.O(CH_2CH_2)_2O$. $(1\text{-}C_{10}H_7)_2BOH$ in $Et_2O$ forms a dioxane adduct, m. 130-1°, which with BuLi gave $(1\text{-}C_{10}H_7)_2BOLi.O(CH_2CH_2)_2O$. Treatment of $(1\text{-}C_{10}H_7)_2BOLi$ with $Me_2SO_4$ in $C_6H_6$ gave 72.3% $(1\text{-}C_{10}H_7)_2BOMe$, m. 101-3°. $(1\text{-}C_{10}H_7)_2BOLi$ and MeOH in $Et_2O$ gave in 15 min. $(1\text{-}C_{10}H_7)_2B(OMe)OH.Li.Et_2O$.

Magnetic susceptibility of some oxalate complexes of tetravalent uranium. T. G. Aminov, V. V. Zelentsov and I. A. Savich (Phys.Tech.Inst., Moscow). Doklady Akad. Nauk S.S.S.R. 128, 533-5(1959).

The following av. values of effective magnetic moment and Weiss constants were detd. conventionally: $K_4[U(C_2O_4)_4].5H_2O$ 3.62 and 60; $Ba_2[U(C_2O_4)_4].6H_2O$ 3.60 and 132; $Cd_2[U(C_2O_4)_4].7H_2O$ 3.85 and 117. Variation of susceptibility with temp. is shown by suitable curves and all the above salts are found to obey the Curie-Weiss law above 195°K. At lower temp. the deviations are caused by formation of low temperature magnetic anomalies and the susceptibility rises more slowly with declining temp. than expected. The effective moments, above, idnicate the state of $^3H_4$ for U, with the 2 unpaired electrons being in the 5f level.

// Zamm.

Some rules of polymerization of propylene with the catalytic system of $TiCl_4$+$AlR_3$.

A. V. Topchiev, B. A. Krentsel and L. G. Sidorova. Doklady Akad. Nauk S.S.S.R. 128, 732-5 (1959).

Polymerization of $C_3H_6$ with $TiCl_4$-$(iso\text{-}Bu)_3Al$ was examined in detail. The chain polymerization process yields within 17 sec. of initiation a polymer with high mol. wt. which remains nearly unchanged over the continued polymerization period of 1.5 hrs. Since the catalyst gradually loses its effectiveness, the rate of reaction declines with time ( shown graphically ), but if $R_3Al$ is gradually added to the system over several hrs. the activity of the system remains at high level and the polymer yield is raised. Addn. of $O_2$ raises the yield to a max. at about 0.026 vol.% $O_2$, after which further addn. of $O_2$ has a negative effect on the yield. Characteristic viscosity of the polymer declines steadily with elevation of temp. of polymerization ( 25-80°). It is suggested that the solid phase of the catalyst present in the reaction zone aids the stereospecificity of the polymerization.

Organozinc compounds of $Ar_2Zn$ class and their dioxanates.

L. Ya. Karpov, L. V. Abramova and V. I. Kochetkov (L.Ya.Karpov Phys. Chem. Inst., Moscow). Doklady Akad. Nauk ...S.S.R. 128, 320-2 (1959). cf. 124, 502(1959).

All expts. described below were run under inert atm. To a well stirred mixt. of 18.8 g. solid PhLi and 14.8 g. dry $ZnCl_2$ powdered under A, there was added 150 ml. xylene, followed by 30 ml. $Et_2O$ ( exothermic ) and the mixt. heated 5-5.5 hrs. at reflux; the soln. was filtered at 70-80° from Li halide ppt. and the filtrate evapd. in part to yield 83.3% colorless crystalline $Ph_2Zn$, m. 105°. Treated with dioxane this gave $Ph_2Zn.C_4H_8O_2$, crystalline solid, sol. in dioxane and $Et_2O$; it is decompd. by $H_2O$ or EtOH. Similarly there was prepd. 71% $(o\text{-}MeC_6H_4)_2Zn$, m. 69-71°; 45% $(p\text{-}MeC_6H_4)_2Zn$, m. 169-70° (dioxanate, a colorless crystalline solid); $(1\text{-}C_{10}H_7)_2Zn$, 49.5%, dec. 200° (dioxanate, colorless solid).

Germanium

Addition of trichlorogermanium to acetylene, olefins and their derivatives in the absence of catalysts.

A. D. Petrov, V. F. Mironov and N. C. Dzhurinskaya (N.D.Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R., 128, 302-4 (1959).

cf. Rochow et al J.Am.Chem.Soc. 76, 5878(1954)

Passage of a rapid stream of HCl through 50 g. particulated Ge and 10 g. pptd. Cu at 450° gave 73% $HGeCl_3$, b. 77-8°. This ( 18 g.) added to 5.5 g. $CH_2$:CHCN at 60-70° ( exothermic ) gave 53% $Cl_3GeCH_2CH_2CN$, $b_{22}$ 135°, m. 37.7°. Similarly $CH_2$:$CHCH_2Cl$ gave 77.4% $Cl_3Ge(CH_2)_3Cl$, $b_{20}$ 105°, $n_D^{20}$ 1.5070, $d_{20}$ 1.6636. $CH_2$:$MeCH_2Cl$ gave 53.3% $Cl_3GeCH_2CHMeCH_2Cl$, $b_{11}$ 90-3°, 1.5000, 1.5758 $CH_2$:$CHSiCl_3$ gave 33% $Cl_3SiCH_2CH_2GeCl_3$, $b_{15}$ 130°, m. 35°. Passage of $C_2H_2$ into $HGeCl_3$ until the exothermic reaction ceased, gave 90% $Cl_3GeCH_2CH_2GeCl_3$, $b_{12}$ 130-1°, m. 56°. Similar reaction with $C_2H_4$ gave 55% $EtGeCl_3$, $b_{761}$ 141.5° 1.4745, 1.6091. 1-Octene gave 55% $n\text{-}C_8H_{17}GeCl_3$, $b_{15}$ 130°, 1.4720, 1.2712. $CH_2$:$CHCH_2OAc$ gave 10.8% $Cl_3GeCH_2CH_2CH_2O_2CMe$, $b_{12}$ 127-80, 1.4855, 2.5392. $CH_2$:$CHCl$ gave 32.5% $Cl_3GeCH_2CH_2Cl$, $b_{15}$ 75°, 1.5092, 1.7637. $Cl_3SiCH$:$CHCl$ gave 52% $Cl_3GeCHClCH_2SiCl_3$, $b_{13}$ 129°, 1.5268, 1.8350. In none of the above addn. reactions was it necessary to add any catalysts or to heat the mixts. in autoclaves. Evidently $HGeCl_3$ has more pronounced additive properties in respect to unsatd. bonds than displayed by $HSiCl_3$.

Arsenic

Thermal decomposition of organic compounds of pentavalent arsenic.

G. Kamai and B. A. Chernokal'skii (S.M.Kirov Chem. Technol. Inst., Kazan).

Doklady Akad. Nauk S.S.S.R. 128, 299-301 (1959).

cf. Lunn et al. J.Chem.Soc. 1949,71.

Pyrolyses of the following substances were performed in distn. app. at 200-20°. $PrAs(O)(OEt)_2$ ( $b_{11}$ 121.5-4°, $d_{20}$ 1.2455, $n_D^{20}$ 1.4520 ) was 40.7% unchanged and gave 11.2% $PrOAs(OEt)_2$, $b_{10}$ 56-9°, 1.1623, 1.4413. $PrAs(O)(OPr)_2$ similarly gave 8.4% PrOH. $PrAs(O)(OBu)_2$ gave 17.1% BuOH, 5.7% $PrAs(OBu)_2$, $b_{12}$ 111-15°, 1.0573, 1.4523 and 2.1% $C_{11}H_{25}O_3As$, $b_{11}$ 121-5°, -, 1.4496. $MeAs(O)(OBu)_2$ gave 9.8% BuOH and 13.5% $MeAs(OBu)_2$, $b_{13}$ 93-5°, 1.0846, 1.4515. $EtAs(O)(OBu)_2$ gave 15.5% BuOH and 19.6% $EtAs(OBu)_2$, $b_{13}$ 103-6°, 1.0727, 1.4534. The latter reaction also gave an unidentified carbonyl compound. Oxidation of $R_2AsOR$ with $SeO_2$ gave $R_2As(O)OR$. Thus were prepd.: from $Et_2AsOEt$ - 1.5% $Et_2AsO_2H$, m. 136-7°, and 2.1% $Et_2AsOEt$, b. 140-1°, $d_{20}$ 1.1148, $n_D^{20}$ 1.4600; from $Et_2AsOPr$ - 16.6% PrOH, 2.7% $Et_2AsO_2H$, m. 135-7°, and 8.9% $Et_2AsOPr$, $b_{13}$ 54.5-7°, 1.0904, 1.4621; from $Et_2AsOBu$ - 12.1% $Et_2As(O)OBu$, $b_4$ 130-30.5°, 1.1922, 1.4721, 11.9% $Et_2AsO_2H$ and 2% $EtAs(OBu)_2$, $b_{11}$ 98.5-101°, -, 1.4522; from $MeBuAsOEt$ - 26% $MeBuAs(O)OEt$, $b_2$ 110-11°, 1.3365, 1.4739 and 11.1% $MeBuAsO_2H$, m. 116-8°; from $MeBuAsOBu$ - 1.9% BuOH, 24.9% $MeBuAs(O)OBu$, $b_3$ 133-4°, 1.1507, 1.4676, and 5.5% $MeBuAsO_2H$, m. 126-7°. Thus the conversion of $R_2AsO_2R$ to $R_2AsOR$ is very facile. The latter esters are readily hydrolyzed with $H_2O$ and atm. moisture. Atomic refraction of As in these compds. is estd. at 8.19. Pyrolysis of $R_3AsO$ gave: from $Et_3AsO$ 2.9% EtOH, 54.4% $Et_3As$; from $Pr_3AsO$ 5.9% PrOH and 35.8% $Pr_3As$; from $Me_2BuAsO$ 23.7% $Me_2BuAs$, b. 133-5°, 1.0560, 1.4673 and 1.9% $MeBuAs(OBu)$, $b_{11}$ 33-5°, -, 1.4611; from $MeBu_2AsO$ 3.9% PrCHO, 8% BuOH, 14.9% $MeBu_2As$, b. 76-6.5°, 1.0103, 1.4724, 2.5% $Bu_3As$, $b_{10}$ 114-6°, 0.9886, 1.4716, and 0.8% $Bu_2As(OMe)$, $b_{13}$ 86-7.5°, -, 1.4685.

Determination of organoaluminum compounds by the indicator method.
G. A. Razuvaev and A. I. Grasevskii. Doklady Akad. Nauk S.S.S.R. 128, 309-11 (1959).

$AlR_3$ and their halogen derivs. may be detd. by adding their soln. in O-free MePh to soln. of Methyl violet in $(CH_2Cl)_2$. The color changes from violet to yellow or green; addn. of an org. base reverts the color back to violet. Compounds of types $R_2AlOR$ or $RAl(OR)_2$ do not produce this color change, possibly owing to screening of their 3p level electrons by the unshared O electron pairs. Titration of $R_3Al$ and their halogen analogs with org. bases such as BuOAc, EtOAc, $Me_2NPh$, $Et_2O$, pyridine results in a clean endpoint when indicators such as Methyl violet, Crystal violet of Gentian violet are used. The titration curves resemble those of strong-acid strong-base titration curves. $Me_2NPh$ reacts with such Al compds. in 1:1 ratio. $Et_2AlBr$ and $EtAlCl_2$ differ in acid strength from $Ph_3Al$ and $Ph_2AlBr$. $Et_2AlBr$ behaves like a dibasic acid. It is possible to titrate $Et_2AlCl$ and $EtAlCl_2$ separately in a mixt. On the basis of detn. of acid strengths by Hantzsch's method ( Ber. 62, 975 (1929)) the following ascending series of acid strength was established: $Et_3Al$, $Et_2AlCl$, $Et_2AlBr$, $EtAlCl_2$. The solns. for the titrations must be dil. as solns. with 30-40% $R_3Al$ destroy the indicators. MePh, xylene, petroleum fraction and heptane may be used as solvents.

**Synthesis of polyorganostannoxanes.**

M. M. Koton and T. M. Kiseleva (High Polymer Inst., Leningrad). Doklady Akad. Nauk S.S.S.R. 130, 86-7 (1960).

Heating a 1:1 molar mixt. of $(EtO)_4Sn$ with iso-$Bu_2Sn(OAc)_2$ ($b_{10}$ 140-1°) 28 hrs. at 140° in inert atm. gave 74.6% EtOAc and a residue of yellowish insol. solid, does not m. 250°, contg. 58% Sn; extn. with $C_6H_6$ gave a yellowish polymer $C_{52}H_{120}O_{15}Sn_8$, m. 70-5°, which is hydrolyzed by $H_2O$ to a colorless insol. and infusible solid $C_{32}H_{74}O_{10}Sn_8$. Apparently the sol. polymer was $HO(SnR_2OSnO)_nOH$. Similarly $(EtO)_4Sn$ and $Bu_2Sn(OAc)_2$ ($b_{10}$ 146-7°) gave an insol. solid contg. 57% Sn and a sol. polymer, m. 60-70°, whose mol. wt. was about 2000.

tin