643. *Organogermanium Compounds. Part I. Preparation of Substituted Triethyl- and Tricyclohexyl-phenylgermanes.*

By C. EABORN and K. C. PANDE.

Monosubstituted phenyltricyclohexylgermanes have been made from chlorotricyclohexylgermane and aryl-lithium compounds in benzene. Similar aryltriethylgermanes, and also mesityl-, and 1- and 2-naphthyl-triethylgermane, have been made from bromotriethylgermane and an aryllithium compound in ether, an arylmagnesium halide in ether, or an aryl halide and sodium in boiling toluene.

There is a linear relation between the refractive indices of aryltriethylgermanes and the analogous aryltrimethylsilanes.

THIS paper describes the preparation of a range of aryl-triethyl- and -tricyclohexylgermanes required for kinetic studies soon to be reported.

The compounds $X\cdot C_6H_4\cdot Ge(C_6H_{11})_3$, where X = H, *m*-Me, *p*-Me, *p*-Et, *p*-Pr^i, *p*-Bu^t, *p*-NMe$_2$, *p*-OMe, and *p*-Cl, were made from chlorotricyclohexylgermane and the appropriate aryl-lithium in boiling benzene (cf. ref. 1).

The compounds $X\cdot C_6H_4\cdot GeEt_3$, where X = H, *p*-Me, *p*-Pr^i, *p*-Bu^t, *p*-OMe, *m*-Cl, *p*-Cl, and *p*-F, were made from bromotriethylgermane and the appropriate arylmagnesium bromide in ether. Triethylphenylgermane prepared by this method could not be freed from biphenyl, but a pure product was obtained from bromotriethylgermane and phenyllithium prepared by cross-metallation of bromobenzene in ether. Triethylphenyl- and triethyl-*p*-tolyl-germane have been prepared previously from the aryltrichlorogermane and ethylmagnesium chloride.[2]

The compounds $X\cdot C_6H_4\cdot GeEt_3$, where X = *m*-Bu^t, *p*-Ph, *o*-NMe$_2$, *p*-NMe$_2$, *o*-OMe, *m*-OMe, *p*-OPh, *p*-CH$_2$SiMe$_3$, *p*-Br, and *p*-I, and also triethyl-2,4,6-trimethylphenylgermane, were made from bromotriethylgermane and the appropriate aryl-lithium in ether. *p*-Bromophenyltriethylgermane has been prepared previously, in low yield and impure, from bromotriethylgermane and *p*-bromophenylmagnesium bromide;[3] use of *p*-bromo- or *p*-iodo-phenyl-lithium made by cross-metallation of *p*-dibromo- or *p*-di-iodo-benzene with a one-molar proportion of n-butyl-lithium, has given pure *p*-bromo- or *p*-iodo-phenyltriethylgermane in 80% yield.

---

[1] Johnson and Nebergall, *J. Amer. Chem. Soc.*, 1949, **71**, 1720.
[2] Bauer and Burschkies, *Ber.*, 1933, **66**, 1156.
[3] Chatt and Williams. *J.*, 1954. 4403.

The compounds $X{\cdot}C_6H_4{\cdot}GeEt_3$, where X = *p*-Et, *o*-Me, *m*-Me, *o*-Ph, and *p*-$O{\cdot}SiMe_3$, were made by Wurtz–Fittig synthesis involving bromotriethylgermane and an aryl bromide or chloride in boiling toluene. This method also gave 1- and 2-naphthyltriethylgermane.

The preparation of bromotriethylgermane from tetraethylgermane [4] has been improved.

A precise relationship exists between the refractive indices of the aryltriethylgermanes prepared and analogous aryltrimethylsilanes,[5] *viz.*, $G = 0{\cdot}800S + 0{\cdot}320$, where G and S are the values of n_D^{20} for corresponding germanium and silicon compounds. The average error in G for the 1- and 2-naphthyl compounds and for the compounds $X{\cdot}C_6H_4{\cdot}MR_3$, where X = H, *m*-Me, *p*-Me, *p*-F, *m*-Cl, *p*-Cl, *p*-I, *p*-$O{\cdot}SiMe_3$, *m*-OMe, *p*-OMe, *p*-OPh, is $\pm 0{\cdot}0010$. The relation can be used as a check on the purity of specimens of either class of compound in cases of doubt; thus when for X = Br one uses the value of n_D^{20} for a sample of *p*-bromophenyltrimethylsilane which was believed [5b] to be impure, the deviation in G is $+0{\cdot}0037$. For the 1-naphthyl and the *o*-tolyl compound the deviations are $-0{\cdot}0042$ and $-0{\cdot}0028$ respectively; we cannot say at this stage whether the relation fails for *ortho*-substituents or whether some of the samples were impure.

EXPERIMENTAL

Fractional Distillations.—A precision-made Vigreux column of *ca.* 15 theoretical plates was used.

Chlorotricyclohexylgermane.—This compound, b. p. 185°/1 mm., m. p. 96°, was prepared in 80% yield from tetrachlorogermane and cyclohexylmagnesium chloride in ether.[6]

Bromotriethylgermane.—Kraus and Flood's method for making this compound, which took 6 days,[4] was modified by adding the bromine all at once and using a higher reaction temperature, as follows. Bromine (37 g.) in anhydrous ethyl bromide (50 ml.) was added all at once to tetraethylgermane (43 g.). A vigorous reaction began after a short time, and was controlled by ice-cooling. When this reaction subsided the mixture was kept at 40—50° for 24 hr., during which almost all the bromine disappeared. Fractionation gave bromotriethylgermane (44 g., 80%), b. p. 191°.

Substituted Phenyltricyclohexylgermanes.—Chlorotricyclohexylgermane (0·015 mole) in benzene (100 ml.) was added to a solution of the aryl-lithium, prepared from the appropriate aryl bromide (0·04 mole) and lithium (0·10 g.-atom) in ether (50 ml.) [except for *p*-chlorophenyllithium, which was made from *p*-bromochlorobenzene (0·04 mole) and n-butyl-lithium (0·04 mole) in ether (50 ml.)]. The ether was distilled off and the residue was boiled under reflux for 1—2 hr. Excess of lithium was removed by filtration, and dilute hydrochloric acid (or water in the case of the *p*-NMe_2 compound) was added, with the usual precautions, to the filtrate. The organic layer was separated, washed, and dried (Na_2SO_4). The solvent was removed, and the residue recrystallised from ethanol to give the aryltricyclohexylgermane (see Table 1), $X{\cdot}C_6H_4{\cdot}Ge(C_6H_{11})_3$, in fine white crystals.

TABLE 1. *Aryltricyclohexylgermanes.*

X in $X{\cdot}C_6H_4$	Yield (%)	M. p.	Found (%) C	Found (%) H	Required (%) C	Required (%) H
m-Me	90	124°	72·6	9·6	72·7	9·8
p-Me	86	135	72·7	9·8	72·7	9·8
p-Et	40	138	73·3	10·0	73·1	10·0
p-Pr^i	80	129·5	73·3	9·8	73·5	10·05
p-Bu^t	87	159·5	73·5	10·0	73·9	10·2
p-OMe	84	132·5	70·0	9·3	70·0	9·4
p-Cl	66	135	66·5	8·7	66·4	8·5
p-NMe_2	78	190	70·8	9·8	70·8	9·6
H (cf. ref. 1)	90	210	—	—	—	—

---

[4] Kraus and Flood, *J. Amer. Chem. Soc.*, 1932, **54**, 1635.

[5] (*a*) Eaborn and Webster, *J.*, 1960, 179; Deans and Eaborn, *J.*, 1959, 2299; Deans, Eaborn, and Webster, *ibid.*, p. 3031; Eaborn, Lasocki, and Webster, *ibid.*, p. 3034; Eaborn, *J.*, 1956, 4858; (*b*) Eaborn and Webster, *J.*, 1957, 4449.

[6] Bauer and Burschkies, *Ber.*, 1932, **65**, 956.

Preparation of Aryltriethylgermanes from Aryl-lithium Compounds.—Bromotriethylgermane (0·05 mole) in ether (50 ml.) was added, at such a rate as to maintain gentle reflux, to a solution of the appropriate aryl-lithium prepared from the aryl bromide (0·075 mole) and lithium (0·2 g.-atom) in ether (100 ml.) [except for *p*-bromo- and *p*-iodo-phenyl-lithium, which were made from *p*-dibromo- or *p*-di-iodo-benzene (0·07 mole) and n-butyl-lithium (0·07 mole) in ether (100 ml.) [7]]. The mixture was refluxed for 1—3 hr., excess of lithium was filtered off, and (except in the preparation of the *o*- and *p*-NMe_2 compounds, for which water was used) dilute hydrochloric acid was added to the filtrate with the usual precautions. The ethereal layer was separated, washed, and dried (Na_2SO_4), and the ether was removed. The residue was fractionated to give the *aryltriethylgermane* (see Table 2), $X{\cdot}C_6H_4{\cdot}GeEt_3$.

TABLE 2. *Aryltriethylgermanes* (*cf. also Tables* 3 *and* 4).

X in $X{\cdot}C_6H_4$	Yield (%)	B. p./mm.	n_D^{20}	Found (%) C	Found (%) H	Required (%) C	Required (%) H
m-Bu^t	92	116—117°/4—5	1·5050	65·8	9·9	65·5	9·55
p-$CH_2{\cdot}SiMe_3$	85	135—136°/3—4	1·5088	59·1	9·5	59·2	9·4
p-Ph	87	158—159°/0·7	1·5780	69·5	8·0	69·1	7·7
o-OMe	86	128·5—129°/7	1·5203	58·5	8·6	58·5	8·3
m-OMe	85	128·5°/6	1·5205	58·7	8·5	58·5	8·3
p-OPh	89	179°/3	1·5581	65·9	7·5	65·7	7·3
p-Br	83	134·5°/4—5	1·5452	45·8	6·1	45·6	6·1
p-I	80	127—128°/2	1·5724	39·9	5·25	39·7	5·3
o-NMe_2 [a]	78	118°/3—4	1·5210	60·3	9·2	60·1	9·0
p-NMe_2 [b]	87	149°/4·5	1·5438	59·8	9·0	60·1	9·0

[a] Found: N, 5·3. $C_{14}H_{25}NGe$ requires N, 5·0%. [b] Found: N, 4·8.

Triethyl-2,4,6-*trimethylphenylgermane*, b. p. 152°/9 mm., n_D^{20} 1·5333, was made similarly in 90% yield (Found: C, 64·8; H, 9·6. $C_{15}H_{26}Ge$ requires, C, 64·6; H, 9·5%)

Triethylphenylgermane, b. p. 117—118°/13·5 mm., n_D^{20} 1·5147 (Found: C, 60·9; H, 8·55. Calc. for $C_{12}H_{20}Ge$: C, 60·8; H, 8·45%), was made in 93% yield by this method from phenyl-lithium derived from bromobenzene and n-butyl-lithium, and was shown by its ultraviolet absorption to be free from biphenyl.

Preparation of Aryltriethylgermanes from Grignard Reagents.—Bromotriethylgermane (0·05 mole) in ether (100 ml.) was added to the Grignard reagent prepared from the appropriate aryl bromide (0·07 mole) and magnesium (0·075 g.-atom) in ether (100 ml.), and the mixture was refluxed for 2—12 hr. Addition of dilute hydrochloric acid, followed by separation, washing, drying (Na_2SO_4), and fractionation of the ethereal layer gave the *aryltriethylgermane* (see Table 3), $X{\cdot}C_6H_4{\cdot}GeEt_3$.

TABLE 3. *Aryltriethylgermanes* (*cf. also Tables* 2 *and* 4).

X in $X{\cdot}C_6H_4$	Reflux time (hr.)	Yield (%)	B. p./mm.	n_D^{20}	Found (%) C	Found (%) H	Required (%) C	Required (%) H
p-Me	3	65	136°/16	1·5134	62·5	9·0	62·4	8·8
p-Pr^i	4	70	136°/7	1·5095	64·7	9·3	64·6	9·05
p-Bu^t	3	85	125°/2	1·5105	65·6	9·8	65·5	9·55
p-F	2	75	121°/15·5	1·4998	56·9	7·3	56·55	7·5
m-Cl	12	60	132—133°/8	1·5289	53·4	6·9	53·1	7·1
p-Cl	6	60	130°/6	1·5287	53·6	6·9	53·1	7·1

The ultraviolet absorption of triethylphenylgermane, b. p. 122°/22 mm., prepared by this method revealed that biphenyl was present, and this could not be removed by further fractionation.

Preparation of Aryltriethylgermanes by Wurtz–Fittig Synthesis.—A mixture of the aryl chloride (X = *o*-Me, *m*-Me, *p*-Et, *o*-Ph) or bromide (X = *p*-$O{\cdot}SiMe_3$) (0·05 mole) and bromotriethylgermane (0·05 mole) was added carefully with vigorous stirring to sodium (0·11 g.-atom) in boiling toluene (110 ml.). The mixture was kept boiling during the addition, heat being supplied if necessary. The mixture was refluxed and stirred for an additional 1 hr. and then filtered. The filtrate was fractionated to give the *aryltriethylgermane* (see Table 4), $X{\cdot}C_6H_4{\cdot}GeEt_3$.

---

[7] Gilman, Langham, and Moore, *J. Amer. Chem. Soc.*, 1940, **62**, 2327.

TABLE 4. *Aryltriethylgermanes* (*cf. Tables* 2 *and* 3).

X in X·C_6H_4	Yield (%)	B. p./mm.	n_D^{20}	Found (%) C	Found (%) H	Required (%) C	Required (%) H
o-Me	74	126°/11	1·5200	61·9	9·0	62·3	8·8
m-Me	63	128°/12	1·5140	62·5	8·7	62·3	8·8
p-Et	65	131—133°/11—12	1·5136	63·5	9·3	63·6	9·15
o-Ph	55	159°/3	1·5701	69·4	7·7	69·1	7·7
p-OSiMe$_3$	42	126—127°/2	1·5050	55·4	8·7	55·4	8·7

From 1- or 2-bromonaphthalene in the same manner were prepared *triethyl*-1-*naphthyl*- (25%), b. p. 153°/4 mm., n_D^{20} 1·5120 (Found: C, 67·1; H, 7·6. $C_{16}H_{22}Ge$ requires C, 67·0; H, 7·7%), and -2-*naphthyl-germane* (64%), b. p. 151°/3—4 mm., n_D^{20} 1·5785 (Found: C, 67·1; H, 7·7%).

We thank the General Electric Co. Ltd. for a gift of germanium dioxide, and the Royal Society for the loan of apparatus from the Government Grant-in-Aid. The work was supported and sponsored in part by the U.S. Department of Army, through its European Research Office.

THE UNIVERSITY, LEICESTER.

[*Received, March 2nd,* 1960.]