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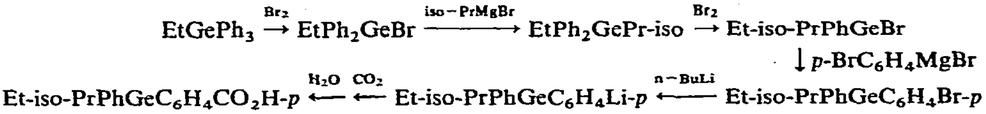
SHORT COMMUNICATION

Organogermanium compounds
IX[1]. The optical resolution of *p*-(ethylisopropylphenylgermyl)benzoic acid

The optical resolution of the acid EtMePhSi$C_6H_4CO_2H$-*p* was reported some years ago[2]. In this paper we describe the preparation and resolution of a rather similar organogermanium compound, the acid Et-iso-PrPhGe$C_6H_4CO_2H$-*p*. The acid was made by the following route:



$$EtGePh_3 \xrightarrow{Br_2} EtPh_2GeBr \xrightarrow{iso-PrMgBr} EtPh_2GePr\text{-}iso \xrightarrow{Br_2} Et\text{-}iso\text{-}PrPhGeBr$$

$$\downarrow p\text{-}BrC_6H_4MgBr$$

$$Et\text{-}iso\text{-}PrPhGeC_6H_4CO_2H\text{-}p \xleftarrow{H_2O} \xleftarrow{CO_2} Et\text{-}iso\text{-}PrPhGeC_6H_4Li\text{-}p \xleftarrow{n-BuLi} Et\text{-}iso\text{-}PrPhGeC_6H_4Br\text{-}p$$

It was then resolved by crystallisation of its (−)-quinine salt from ethanol, the least soluble diastereisomer giving, after hydrolysis, the (+)-*p*-(ethylisopropylphenylgermyl)benzoic acid, m.p. 117–119.5°, $[\alpha]_D^{16}$ +0.48° (*c*, 3.2 in ethanol). The rotation, while small, is in the opposite direction to that of the quinine used, and thus it is clear that at least partial resolution was achieved. The impure (−)-acid, $[\alpha]_D^{23}$ −0.17°, was obtained from the resolution mother liquors.

Experimental

Ethylbromodiphenylgermane. Bromine (31.3 g, 0.19 mole) in ethylene dibromide (50 ml) was added gradually to a hot solution of ethyltriphenylgermane (70 g, 0.19 mole) in ethylene dibromide (400 ml). The reaction mixture was boiled under reflux for 0.5 h then concentrated under reduced pressure, and the residue was fractionated to give ethylbromodiphenylgermane, b.p. 127–129.5°/0.2 mm, n_D^{25} 1.6025 (55.2 g, 78%). (Found: C, 50.1; H, 4.9. $C_{14}H_{15}BrGe$ calcd.: C, 50.05; H, 4.5%.)

Ethylisopropyldiphenylgermane. To the Grignard reagent obtained from magnesium turnings (8.5 g, 0.35 g-atoms) and isopropyl bromide (43.1 g, 0.35 mole) in ether (500 ml) was added a benzene solution of ethylbromodiphenylgermane (55 g, 0.16 mole). The ether was replaced by benzene and the reaction mixture boiled under reflux for 16 h. The usual working-up, as above, gave an oil, which was fractionated to give ethylisopropyldiphenylgermane, b.p. 104–105°/0.15 mm, n_D^{25} 1.5641 (34.1 g, 70%) (lit.[3] b.p. 175–190°). (Found: C, 68.2; H, 7.3. $C_{17}H_{22}Ge$ calcd.: C, 68.3; H, 7.4%.)

Ethylisopropylphenylbromogermane. Ethylisopropyldiphenylgermane (36.3 g, 0.12 mole) was treated with bromine (19.6 g, 0.12 mole) in ethylene dibromide, and concentration of the solution gave an oil, which was fractionated to give ethylisopropylphenylbromogermane; b.p. 75–76°/0.15 mm, n_D^{25} 1.5473 (31 g, 84%) (lit.[3] b.p. 130–135°/13 mm). (Found: C, 43.9; H, 5.6. $C_{11}H_{17}BrGe$ calcd.: C, 43.8; H, 5.6%.)

(p-Bromophenyl)ethylisopropylphenylgermane. After initiation of reaction at room temperature, *p*-dibromobenzene (69.5 g, 0.3 mole) in ether (400 ml) was added, all at once, at −10°, to magnesium turnings (7.15 g, 0.3 g-atom). The reaction mixture was stirred at −5° for 2 h then allowed to warm to room temperature, and the ether

was replaced by toluene. Ethylisopropylphenylbromogermane (30.4 g, 0.10 mole) in toluene (250 ml) was added, and the mixture was refluxed for 15 h with stirring. The usual working-up left an oil, which was heated to 140°/10 mm to expel unreacted *p*-dibromobenzene, and then fractionated to give (*p*-bromophenyl)ethylisopropylphenylgermane, b.p. 128–130°/0.01 mm, n_D^{25} 1.5856 (25.5 g, 69%). (Found: C, 54.0; H, 5.4. $C_{17}H_{21}BrGe$ calcd.: C, 54.0; H, 5.6%.)

p-(Ethylisopropylphenylgermyl)benzoic acid. To n-butyllithium, made from Li (0.23 g, 0.033 g-atom) and 1-bromobutane (3.2 g, 0.023 mole) in ether at −40°, was added, at −15°, (*p*-bromophenyl)ethylisopropylphenylgermane (4.3 g, 0.0113 mole) in ether (30 ml). The reaction mixture was stirred at −10° for 0.5 h, then at room temperature for 3 h. Lithium was filtered off, and the clear filtrate was added dropwise to a slurry of solid carbon dioxide and ether. The mixture was set aside overnight, then acidified with 0.05 *N* hydrochloric acid, and the ethereal layer was separated and repeatedly extracted with 0.2 *N* aqueous sodium hydroxide. The alkaline aqueous extract was acidified with 0.5 *N* hydrochloric acid, and the precipitated acid was taken up in ether. Removal of the ether left a yellow solid (2.0 g), m.p. 110–112.5°, which was crystallised from aqueous ethanol at −5 to −10° to give racemic *p*-(ethylisopropylphenylgermyl)benzoic acid (1.8 g, 47%), m.p. 115.5–117°. (Found: C, 62.8; H, 6.6; equiv. wt, 345. $C_{18}H_{22}GeO_2$ calcd.: C, 63.0; H, 6.4%; equiv. wt, 343.)

Resolution of p-(ethylisopropylphenylgermyl)benzoic acid. *p*-(Ethylisopropylphenylgermyl)benzoic acid (1.40 g, 4.0 mmole) and quinine (1.33 g, 4.0 mmole) were dissolved in ethanol (40 ml) and the solution was allowed to stand in a refrigerator for 7 days. The crystals which separated were filtered off, washed with ethanol, and dried at 20°/0.5 mm, to give the diastereoisomer of m.p. 147.5–148° (0.41 g, 30%), $[\alpha]_D^{16}$ −98.3° (*c*, 0.54 in benzene). (Found: N, 4.1. $C_{38}H_{46}GeN_2O_4$ calcd.: N, 4.2%.) (Further crops of crystals had similar melting points but lower specific rotations.) This salt (0.33 g) was suspended in ether (25 ml), and the mixture was agitated with 0.1 *N* hydrochloric acid. When all the solid had disappeared the ethereal layer was separated and washed with 0.05 *N* hydrochloric acid followed by water. The ether was removed by evaporation, and the residue was dried at 30°/0.5 mm, to give (+)-*p*-(ethylisopropylphenylgermyl)benzoic acid (0.16 g, 93%), m.p. 117–119.5°, $[\alpha]_D^{16}$ +0.48°, (*c*, 3.2 in benzene). The infrared spectrum was identical with that of the racemic acid.

Similar treatment of later crops of the quinine salt gave samples of the acid with lower positive specific rotations. Evaporation of the resolution mother liquors followed by the treatment described above gave a sample of the acid, m.p. 109.5–113°, $[\alpha]_D^{23}$ −0.17° in benzene). (Found: C, 63.0; H, 6.5%.)

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