76. *Organic Compounds of Zirconium. Part VI.* Reactions of Zirconium Tetrachloride and* iso*Propoxide with Fatty Acids.*

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Fatty acids with zirconium tetrachloride give tetracarboxylates directly. With zirconium *iso*propoxide only oxygen-bridged compounds of the type $(R{\cdot}CO_2)_3Zr{\cdot}O{\cdot}Zr(CO_2R)_3$ are obtained. By studying the latter reaction stepwise, we find that it is straightforward to the dicarboxylate stage, after which side reactions occur. A mechanism is suggested.

Although there is much recent work on organic derivatives of zirconium, the only reference to its compounds with monocarboxylic acids is that of Ryan and Plechner[1] who claimed the preparation of zirconium tetra-soaps by the reaction:

$$ZrCl_4 + 4R{\cdot}CO_2H + 2CaCO_3 \longrightarrow Zr(R{\cdot}CO_2)_4 + 2CaCl_2 + 2CO_2 + 2H_2O \quad . \; . \; . \quad (i)$$

On attempting this reaction, we obtained highly hydrolysed derivatives owing to the water produced. Aqueous precipitation methods, even under modified conditions, always yielded hydrolysed products of indefinite composition; zirconium salts, even of strong mineral acids, are readily hydrolysed.

We therefore attempted to prepare zirconium carboxylates in a non-aqueous medium

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* Part V, Kapoor and Mehrotra, *J. Amer. Chem. Soc.*, 1958, **80**, 3569.

[1] Ryan and Plechner, *Ind. Eng. Chem.*, 1934, **26**, 909.

from zirconium tetra*iso*propoxide, which is easily obtainable pure and dissolves freely in benzene.

Zirconium *iso*propoxide and excess of a fatty acid (stearic, palmitic, lauric, and caproic) yield [2] basic tricarboxylates $(R\cdot CO_2)_3Zr\cdot O\cdot Zr(CO_2R)_3$ which are unchanged on repeated crystallisation from dioxan. The reaction was carried out in refluxing benzene under a column so that the *iso*propyl alcohol produced could be removed azeotropically with benzene. The alcohol in the azeotrope was estimated. Even when the ratio zirconium *iso*propoxide : fatty acid was more than 1 : 4, not more than 4·5 moles of alcohol per mole of the crystalline *iso*propoxide $Zr(OPr^i)_4,Pr^iOH$ distilled azeotropically. It thus appeared that the replacement of the fifth alcoholic group might be slow owing to steric hindrance, or that a side reaction occurred owing to which a portion of the replaceable alcohol in the alkoxide could not be distilled. For example, the fact that 4·5 mol. of alcohol are replaced can be explained simply if the main reaction is represented by:

$$\mathrm{2Zr(OPr^i)_4,Pr^iOH + 6R\cdot CO_2H \longrightarrow 2Zr(OPr^i)(R\cdot CO_2)_3 + 8Pr^iOH} \quad \ldots\ldots \quad \mathrm{(ii)}$$

$$\mathrm{Zr(OPr^i)(R\cdot CO_2)_3 + R\cdot CO_2H \longrightarrow Zr(R\cdot CO_2)_4 + Pr^iOH\ (slow)} \quad \ldots\ldots \quad \mathrm{(iii)}$$

$$\mathrm{Zr(OPr^i)(R\cdot CO_2)_3 + Zr(R\cdot CO_2)_4 \longrightarrow (R\cdot CO_2)_3Zr\cdot O\cdot Zr(CO_2R)_3 + R\cdot CO_2Pr^i} \quad \ldots \quad \mathrm{(iv)}$$

The reaction of zirconium tetra*iso*propoxide with palmitic and stearic acids was carried out stepwise:

$$\mathrm{Zr(OPr^i)_4,Pr^iOH + R\cdot CO_2H \longrightarrow Zr(R\cdot CO_2)(OPr^i)_3 + 2Pr^iOH} \quad \ldots\ldots \quad \mathrm{(v)}$$

$$\mathrm{Zr(OPr^i)_4,Pr^iOH + 2R\cdot CO_2H \longrightarrow Zr(R\cdot CO_2)_2(OPr^i)_2 + 3Pr^iOH} \quad \ldots\ldots \quad \mathrm{(vi)}$$

These replacements were rapid and the benzene–*iso*propyl alcohol azeotrope distilled quickly. Tri*iso*propoxyzirconium monostearate and monopalmitate and di*iso*propoxyzirconium distearate and dipalmitate were isolated pure. They are stable to heat under reduced pressure, but are susceptible to atmospheric moisture.

The di-soaps were treated with fatty acids (palmitic or stearic) in the molar ratio 1 : 1. On fractionation almost 1 mol. of alcohol distilled azeotropically, indicating the simple reaction:

$$\mathrm{Zr(OPr^i)_2(R\cdot CO_2)_2 + R\cdot CO_2H \longrightarrow Zr(OPr^i)(R\cdot CO_2)_3 + Pr^iOH} \quad \ldots\ldots \quad \mathrm{(vii)}$$

From the remaining solution, benzene was distilled off under reduced pressure and the solid products were analysed. The zirconium content corresponded to the mono*iso*propoxy-tricarboxylate, but the *iso*propoxy-content was considerably below theoretical. Further the *iso*proxy-content depended on the amount of heating to which the products were subjected. If the mono*iso*propoxytristearate decomposes:

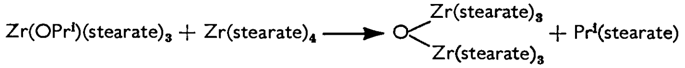
$$\mathrm{Zr(OPr^i)(R\cdot CO_2)_3 = O{:}Zr(R\cdot CO_2)_2 + R\cdot CO_2Pr^i} \quad \ldots\ldots\ldots\ldots \quad \mathrm{(viii)}$$

the analytical results could be explained. The product from reaction (vii) was treated with dry dioxan; the crystallised zirconium soap on analysis corresponded to a mixture of $ZrO(R\cdot CO_2)_2$ and $Zr(OPr^i)(R\cdot CO_2)_3$. The sweet-smelling dioxan-soluble portion was a mixture of the fatty acid and ester; on analysis a sample conformed with the decomposition (viii).

The isolation of the *iso*propoxyzirconium tristearate is, therefore, only possible by carrying out the reaction at a low temperature:

$$\mathrm{Zr(OPr^i)_4 + 3R\cdot CO_2H \longrightarrow Zr(OPr^i)(R\cdot CO_2)_3 + 3Pr^iOH} \quad \ldots\ldots \quad \mathrm{(ix)}$$

The correctness of the overall reaction mechanism (iv) has been further demonstrated by refluxing an equimolecular mixture of the *iso*propoxyzirconium tristearate and the tetrastearate, whereupon the reaction (x) takes place:



$$\mathrm{Zr(OPr^i)(stearate)_3 + Zr(stearate)_4 \longrightarrow O{<}\begin{matrix}\mathrm{Zr(stearate)_3}\\ \mathrm{Zr(stearate)_3}\end{matrix} + Pr^i(stearate)} \quad \ldots \quad \mathrm{(x)}$$

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[2] Kapoor and Mehrotra, *Chem. and Ind.*, 1958, 68.

Having failed to prepare zirconium tetra-soaps by the above reaction, we tried to make zirconium tetrachloride react with fatty acids (stearic, palmitic, and myristic). Although the tetrachloride is not appreciably soluble in benzene, it slowly reacted with fatty acids when refluxed and hydrogen chloride was freely evolved. Refluxing was continued until this evolution became negligible, and the solution gave colourless crystals of tetra-soaps:

$$\mathrm{ZrCl_4 + 4R{\cdot}CO_2H \longrightarrow Zr(R{\cdot}CO_2)_4 + 4HCl} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(xi)}$$

Repeated crystallisation from benzene did not noticeably change the analysis of the product whose identity is thus confirmed.

Titanium compounds behave similarly.[3]

EXPERIMENTAL

Apparatus.—All-glass apparatus with interchangeable joints was used with care to exclude moisture. All fractionations were carried out in a 60 cm. column packed with Raschig rings and fitted with a total-condensation variable take-off stillhead.

Materials.—Zirconium *iso*propoxide (used as the *iso*propyl alcoholate), prepared by Bradley, Mehrotra, and Wardlaw's method, was repeatedly crystallised from *iso*propyl alcohol [Found: Zr, 23·60; $\mathrm{Pr^iO}$, 76·9. Calc. for $\mathrm{Zr(OPr^i)_4,Pr^iOH}$: Zr, 23·53; $\mathrm{Pr^iO}$, 76·21%]. Zirconium tetrachloride (Merck, resublimed G.R. sample) was a fine, pale yellow powder. The fatty acids (decanoic, lauric, myristic, palmitic, and stearic) were Reagent Grade products of B.D.H. or Kahlbaum. They were repeatedly crystallised, then fractionated under reduced pressure.

Benzene ("AnalaR") was dried by storage and fractionation over sodium. Dioxan (B.D.H., Technical) was refluxed with sodium to remove peroxide and then fractionated.

Analyses.—Zirconium was estimated as oxide by direct ignition. The alcohol content of the benzene–alcohol azeotrope was determined by an oxidimetric method [5] which could be applied directly as benzene did not reduce potassium dichromate at room temperature.

Reaction between Zirconium iso*Propoxide and Excess of Fatty Acids.—Procedure.* The methods of preparation being similar, details are given of one preparation only.

Zirconium iso*propoxide and excess of palmitic acid.* Benzene (80 g.) was added to zirconium tetra*iso*propoxide (2·59 g.) and palmitic acid (9·6 g.). The mixture was refluxed under a column (bath temp., 120—130°). About 20 c.c. of the distillate, collected at 71—75° during ½ hr., contained 1 g. of *iso*propyl alcohol. The temperature of the distilling liquid rose at this stage and after about 1 hr. became almost steady at 76°. Nearly 20 c.c. of the distillate, collected at 76—80° during about 2 hr., contained 0·6 g. of the alcohol. The temperature of the distilling liquid eventually became constant at 80° and benzene was collected under a reflux-ratio of 1 : 20. The residue was a colourless mobile solution in benzene, from which a white solid was obtained after removal of the benzene at 40° (bath)/2 mm.

The total *iso*propyl alcohol in the azeotrope was 1·6 g. (Calc. for 4 mol.: 1·9 g.). The product was refluxed with dry dioxan (50 c.c.) for nearly 5 min. at 120° (bath), giving a clear solution which, on cooling, gave white crystals which were washed with dry dioxan and dried [60° (bath)/2 mm.] for 2 hr. [Found: Zr, 10·52%. Calc. for $\mathrm{(C_{15}H_{31}{\cdot}CO_2)Zr{\cdot}O{\cdot}Zr(CO_2C_{15}H_{31})}$: Zr, 10·45%].

The dioxan filtrate contained 2·48 g. of free fatty acid and 1·0 g. of *iso*propyl palmitate which were respectively estimated by direct titration with alkali and after hydrolysis in boiling alkali. The quantities expected are 2·5 g. and 1·02 g. if the reaction was:

$$\mathrm{2Zr(OPr^i) + 7R{\cdot}CO_2H \longrightarrow (R{\cdot}CO_2)_3Zr{\cdot}O{\cdot}Zr(CO_2R)_3 + R{\cdot}CO_2Pr^i + 7Pr^iOH}$$

Zirconium iso*propoxide and excess of stearic acid.* Zirconium *iso*propoxide (1·34 g.) in benzene (80 g.) and stearic acid (4·42 g.) were treated as above [Found: Zr, 9·71. Calc. for $\mathrm{(C_{17}H_{35}{\cdot}CO_2)_3Zr{\cdot}O{\cdot}Zr(CO_2C_{17}H_{35})_3}$: Zr, 9·61%]. Total *iso*propyl alcohol found in the azeotrope was 0·93 g. against 1·03 g. required for 5 mol.

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[3] Pande and Mehrotra, *Z. anorg. Chem.*, 1957, **290**, 87, 95; 1957, **291**, 87; *J. prakt. Chem.*, 1957, **5**, 101.

[4] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027.

[5] Mehrotra, *J. Indian Chem. Soc.*, 1953, **30**, 588.

Zirconium iso*propoxide and excess of lauric acid.* Zirconium *iso*propoxide (1·29 g.) and lauric acid (3·02 g.) in benzene (58 g.) gave a distillate (about 25 g.) between 72—80°. The remaining benzene solution was treated as above, yielding a gum which did not crystallise from dioxan. The gum was heated at 200° (bath)/0·5 mm. for 1 hr. Repetition of the treatment with dioxan, gave a white product [Found: Zr, 12·78. Calc. for $(C_{11}H_{23}\cdot CO_2)_3Zr\cdot O\cdot Zr(CO_2C_{11}H_{23})_3$: Zr, 13·06%].

Zirconium iso*propoxide and excess of decanoic acid.* Zirconium *iso*propoxide (2·13 g.) and decanoic acid (4·16 g.) were allowed to react in benzene (60 g.) as above. The product (a yellow viscous liquid) was treated as for lauric acid [Found: Zr, 13·96%. Calc. for $(C_9H_{19}\cdot CO_2)_3Zr\cdot O\cdot Zr(O_2C\cdot C_9H_{19})_3$: Zr, 14·84%.

Reaction between Zirconium iso*Propoxide and Fatty Acids in Different Molar Ratios.*—*Tri*iso*propoxyzirconium monostearate.* Benzene (56 g.) was refluxed (bath, 130°) with zirconium *iso*propoxide (1·80 g.) and stearic acid (1·17 g. (molar ratio 1 : 1). The benzene–*iso*propyl alcohol azeotrope collected in 1 hr. contained 0·49 g. of alcohol (Calc., 0·49 g.). A paste was obtained [Found: Zr, 16·49; OPr^{i}, 32·0. Calc. for $Zr(OPr^i)_3(C_{17}H_{35}\cdot CO_2)$: Zr, 16·52: OPr^{i}, 32·15%].

*Tri*iso*propoxyzirconium monopalmitate.* Refluxing of zirconium *iso*propoxide (1·41 g.) and palmitic acid (0·93 g.) (molar ratio 1 : 1) in benzene (60 g.) as above gave 0·42 g. of *iso*propyl alcohol in the azeotrope, and a residue [Found: Zr, 17·21; OPr^{i}, 33·8. Calc. for $Zr(OPr^i)_3(C_{15}H_{31}\cdot CO_2)$: Zr, 17·41; OPr^{i}, 33·82%].

*Di*iso*propoxyzirconium distearate.* Zirconium *iso*propoxide (2·19 g.) and stearic acid (3·21 g.) (molar ratio 1 : 2) were refluxed (bath, 140°) in benzene (55 g.). The azeotrope, fractionated and collected within 1 hr., contained 1·0 g. of *iso*propyl alcohol (Calc., 1·02 g.) [Found in residue: Zr, 11·28; OPr^{i}, 15·0. Calc. for $Zr(OPr^i)_2(C_{17}H_{35}\cdot CO_2)_2$: Zr, 11·75; OPr^{i}, 15·21%].

*Di*iso*propoxyzirconium dipalmitate.* Zirconium *iso*propoxide (2·03 g.) and palmitic acid (2·68 g.) (molar ratio 1 : 2) in benzene as above gave an azeotrope containing 0·940 g. of *iso*-propyl alcohol (Calc., 0·944 g.) and a viscous mass (3·88 g.) which became semi-solid on long storage [Found: Zr, 12·63; OPr^{i}, 16·30. Calc. for $Zr(OPr^i)_2(C_{15}H_{31}\cdot CO_2)_2$: Zr, 12·66; OPr^{i}, 16·38%].

Zirconium iso*propoxide and stearic acid* (*molar ratio* 1 : 3). Zirconium *iso*propoxide (2·05 g.) and stearic acid (4·53 g.) in benzene (65 g.) gave on refluxing under the column a distillate (*ca.* 25 c.c.) at 72—80° containing 1·25 g. of *iso*propyl alcohol (Calc., 1·27 g.). The remaining solution in benzene, treated as above, gave a white product [Found: Zr, 9·10; OPr^{i}, 1·0. Calc. for $Zr(OPr^i)(C_{17}H_{35}\cdot CO_2)_3$: Zr, 9·10; OPr^{i}, 5·9%] which when refluxed with dry dioxan (20 c.c.) (bath, 120°) for 10 min. gave a white mass (Found: Zr, 12·40; OPr^{i}, negligible).

Zirconium iso*propoxide and palmitic acid* (*molar ratio* 1 : 3). Zirconium *iso*propoxide (2·27 g.) and palmitic acid (4·52 g.) in refluxing benzene (60 c.c.) gave a distillate (*ca.* 25 c.c.) at 72—80° containing 1·37 g. of *iso*propyl alcohol (Calc., 1·40 g. for the replacement of 4 mol.) and a residue [Found: Zr, 9·97; OPr^{i}, 1·8. Calc. for $Zr(OPr^i)(C_{15}H_{31}\cdot CO_2)_3$: Zr, 9·95; OPr^{i}, 6·6%] which was treated with dioxan (Found: Zr, 12·87; OPr^{i}, 1·6%).

*Di*iso*propoxyzirconium dipalmitate and palmitic acid* (1 *mol.*). Palmitic acid (0·76 g.) was refluxed with di*iso*propoxyzirconium dipalmitate (2·16 g.) in benzene (50 c.c. (bath, 130°). The azeotrope, collected in 1 hr., contained 0·17 g. of *iso*propyl alcohol (Calc. 0·18 g.). Removal of excess of benzene under reduced pressure left a low-melting solid (Found: Zr, 10·12; OPr^{i}, 1·76%) which was treated with dioxan (Found: Zr, 12·76%).

*Mono*iso*propoxyzirconium Tristearate.*—Zirconium tetra*iso*propoxide (2·87 g.; 3 mol.) was added to stearic acid (7·48 g.; 1 mol.) in benzene (60 c.c.). The volatile fractions were removed [30° (bath)/2 mm. in 3 hr. to leave a residue [Found: Zr, 9·19; OPr^{i}, 5·7. Calc. for $Zr(OPr^i)(C_{17}H_{35}\cdot CO_2)_3$: Zr, 9·12; OPr^{i}, 5·9%] which, after refluxing with dry benzene (30 c.c.) for $\frac{1}{2}$ hr. at 110°, removal of volatile fractions (2 mm.) for 2 hr., and refluxing with dry dioxan (20 c.c.), gave crystals (Found: Zr, 12·40; OPr^{i}, 0·6%).

*Reaction of Mono*iso*propoxyzirconium Tristearate with Zirconium Tetrastearate in Dry Dioxan.*—Dioxan (30 c.c.) was heated (bath, 120°) with mono*iso*propoxyzirconium tristearate (0·94 g.) and zirconium tetrastearate (1·14 g.) (molar ratio of 1 : 1). Cooling of the clear solution gave a white mass {Found: Zr, 9·61. Calc. for $O[Zr(C_{17}H_{35}\cdot CO_2)_3]_2$: Zr, 9·61%} which did not recrystallise from benzene.

Zirconium Tetra-soaps.—*Zirconium tetrapalmitate.* Palmitic acid (9·54 g.; 4·5 mol.) and the suspension of zirconium tetrachloride (1·92 g.; 1 mol.) in benzene (44 g.) were refluxed for 14 hr. (bath, 100°) until evolution of hydrogen chloride almost ceased and a clear solution was obtained. On storage overnight, a white mass separated. This was recrystallised from benzene (25 c.c.), filtered off, washed, and dried (40°/2 mm.) for 2 hr. [Found: Zr, 8·13. Calc. for $Zr(C_{15}H_{31}\cdot CO_2)_4$: Zr, 8·19%].

Zirconium tetrapalmitate (*ca.* 2 g.) was refluxed with dry dioxan (20 c.c.) for about 10 min. (bath, 120°). Cooling of the clear solution gave white crystals which were filtered off, washed with dry dioxan, and dried (50°/4 mm.) for 2 hr. (yield 1·8 g.) [Found: Zr, 8·29. Calc. for $Zr(C_{15}H_{31}\ CO_2)_4$: Zr, 8·19%].

Zirconium tetrastearate. Zirconium tetrachloride (1·31 g.), benzene (52 g.), and stearic acid (7·98 g.) were treated as above. A portion of the crystalline product [Found: Zr, 7·43. Calc. for $Zr(C_{17}H_{35}\cdot CO_2)_4$: Zr, 7·44%] on treatment with dry dioxan gave crystals containing 7·60% of zirconium.

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