

Reactions of Orthoesters of Titanium. III

Reactions of Ethyl and Isopropyl Titanates with α -hydroxy Carboxylic Acids

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Summary

Stepwise replacement of alkyl groups of ethyl and isopropyl titanates by acyl groups of lactic, mandelic, and salicylic acids has been investigated by taking the reactants in predetermined stoichiometric proportions and causing them to react in refluxing benzene. The number of alkyl groups replaced was determined by estimating the alcohol liberated in the reaction and by analysing the reaction product. When the alkyl titanates are acted upon by 2 moles of these acids, salicylic acid liberates 4 moles of alcohol (per mole alkyl titanate) whereas remaining two acids displace only 3 or 3.5 moles of alcohol. Thus di-lactate and mandelate derivatives appear to withhold very firmly the remaining alkoxy group. However, with 3 moles (or higher proportions) of these acids, alkyl titanates yield, in every case, an equimolecular mixture of di- and tri-acylates.

The lactate and mandelate products are white solids, but the salicylates are orange or deep red in colour. Mono-lactate, salicylate and mandelate derivatives are soluble in benzene, whereas the equimolecular mixture of di- and tri-lactate dissolves in water without precipitation of titanium hydroxide.

Alcohol interchange reactions have been widely employed for preparation of higher alkyl ortho-titanates¹), as well as for preparation of mixed alkyl titanates²). The aryl orthotitanates as well as mixed alkyl-aryl orthotitanates have also been prepared by causing the stoichiometric ratios of phenol to react with ethyl and isopropyl titanates²).

Recently, it has been shown that when alkyl titanates are acted upon by aliphatic³) or aromatic⁴) mono-carboxylic acids in stoichiometric ratios the alkyl radical is successively replaced by the acyl groups. However, the number of alkyl radicals which can thus be replaced is

¹) D. C. BRADLEY, R. C. MEHROTRA and W. WARDLAW, J. chem. Soc. London **1952**, 2027.

²) I. D. VARMA and R. C. MEHROTRA, Unpublished results.

³) K. C. PANDE and R. C. MEHROTRA, Z. anorg. allg. Chem. **290**, 87 (1957).

⁴) I. D. VARMA and R. C. MEHROTRA, J. prakt. Chem. (4), **8**, 235 (1959).

generally limited to 3 and in no case the tetra-acylate is produced. The formation of titanium mono-alkoxy tri-acylate proceeds slowly and can be pushed to completion only if the liberated alcohol is continuously removed azeotropically. Further, the triacylate derivative suffers thermal decomposition during the course of formation and hence, the final end-product consists of undecomposed tri-acylate alongwith basic titanium acylate and the corresponding ester.

The physico-chemical studies of the reaction between the α -hydroxy carboxylic acids and metal ions in aqueous solution have revealed that the hydrogen of the hydroxyl group becomes reactive as a result of the chelation and the complex ion dissociates as an acid⁵).

In view of the above, a systematic study of the reactions of salicylic, mandelic and lactic acids with ethyl and isopropyl titanates was undertaken. The reactions were carried out in refluxing benzene and the alcohols produced were removed azeotropically (represented in table 1). A perusal of table 1 reveals that compared to lactic and mandelic acids, salicylic acid is more reactive in as much as its 2 moles can replace all the four alkoxy groups of the alkyl titanates.

Table 1

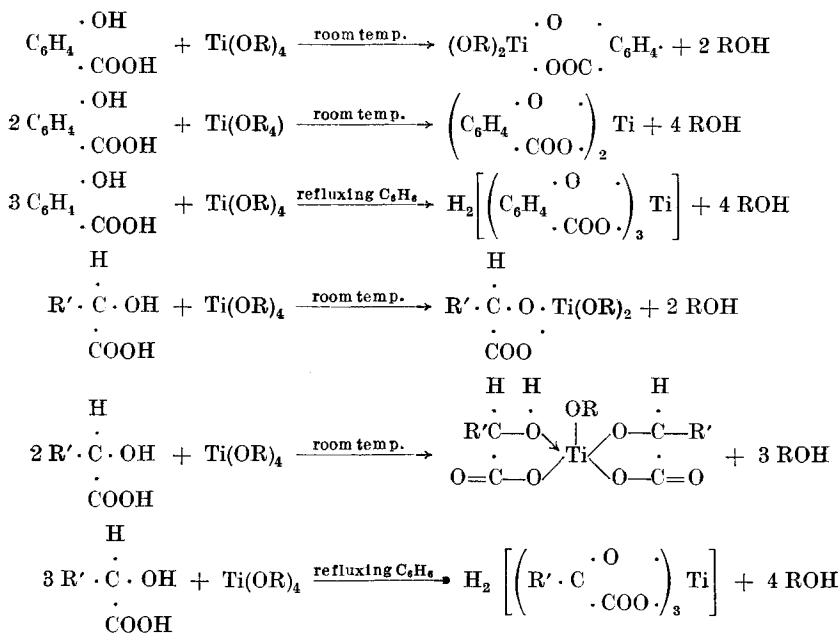
Alkyl titanate:Acid	Alcohol (moles) liberated per mole of alkyl titanate					
	Salicylic Acid		Lactic Acid		Mandelic Acid	
	EtOH	Pr ⁱ OH	EtOH	Pr ⁱ OH	EtOH	Pr ⁱ OH
1:1	2.0	2.0	2.0	1.94	1.61	1.84
1:2	3.71	3.81	3.04	3.37	2.90	2.70
1:3	—	3.83	3.85	—	3.79	—
1:4	3.78	—	—	3.70	3.46	3.66
or more than 4						

The reaction products were freed of the solvent under reduced pressure and were dried at 60–65°/0.5–1.5 mm., after being washed with dry ether. The salicylates are orange to intense red, microcrystalline solids, out of which the mono-salicylate derivatives are soluble in benzene. The mandelates and lactates are white amorphous solids, insoluble in benzene except the corresponding mono-derivatives.

On the basis of the alcohol liberated in the reactions as well as the analyses of the reaction products, the various reactions can be represented

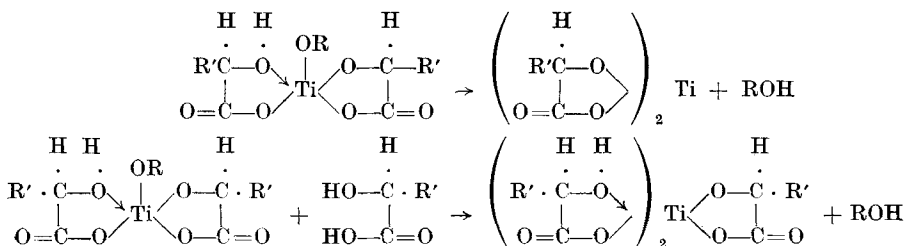
⁵) I. D. VARMA and R. C. MEHROTRA, J. Ind. Chem. Soc. **35**, 381 (1958).

as below :



(R: —OEt or —OPr¹; R': CH₃ or C₆H₅).

The di-lactate or di-mandelate derivatives exhibit a marked tendency of tenaciously withholding one (in some cases 0.5) mole of Pr¹OH or EtOH respectively. The stability of these di-acylates of titanium suggests that the last alkoxy group is replaced with great difficulty. The above is confirmed by attempting to exchange the alkoxy group of these diacylates with a higher alcohol or by causing them to react with additional quantities of corresponding acids, when the remaining alcohol is liberated incompletely, although the insolubility in benzene of these compounds might also be affecting the liberation of alcohol. In the latter case, a mixture of di- and tri-acylates is obtained which may be explained on the basis of the two following reactions occurring simultaneously:



The di- and tri-acylates are also formed when alkyl titanates are acted upon by 3 moles of corresponding acids. Still higher proportions of acid do not appear to affect the course of reaction, except that some of the liberated alcohol undergoes esterification with the excess acid (lactic and mandelic) thus lowering the quantity of the liberated alcohol.

Apparatus

All glass apparatus with interchangeable joints was used and moisture was excluded from all the experiments. A 60 cm. long column packed with Rachig rings and fitted to a total condensation variable takeoff stillhead was used for fractionation.

Reagents

Titanium alkoxides (Peter Spence products) were purified by distillation under reduced pressure. Titanium ethoxide, b. p. 121°/0.8 mm. Anal. Calcd. for $\text{Ti}(\text{Et})_4$: Ti 20.99%, OEt 79.01%, Found: Ti 21.02%, OEt 78.85%.

Titanium isopropoxide, b. p. 80°/2 mm. Anal. Calcd. for $\text{Ti}(\text{OPr}^i)_4$: Ti 16.85%, OPr^i 83.15%; Found Ti 16.88%, OPr^i 83.15%. Benzene (B.D.H., AnalaR) was dried over sodium wire and finally dried azeotropically with ethanol. Ether was dehydrated by distilling it over sodium wire. Lactic, mandelic and salicylic acids (B.D.H., AnalaR) were dried at 50–60° under reduced pressure immediately before use.

Analytical methods

Titanium was estimated by ignition of the compound and weighed as TiO_2 . The ethanol and isopropanol in benzene azeotrope were estimated by oxidation with $\text{N K}_2\text{Cr}_2\text{O}_7$ (in 12.5% H_2SO_4)*.

The mandelate group in the compounds was estimated by its oxidation with excess 0.012 N ceric sulphate solution (in $\text{N H}_2\text{SO}_4$) at 95–100° for 4 mts. and back titration with standard ferrous ammonium sulphate solution, using N phenyl anthranilic acid as indicator. In some cases, a correction for alcohol content of compound was applied by running blanks with identical quantities of alcohol as present in the compounds. It was, however, found that small quantities of alcohol do not interfere with the estimation.

Reactions of titanium ethoxide and salicylic acid

Molar ratio: 1:1

Salicylic acid (2.76 g.) was admitted to a solution of titanium ethoxide (4.56 g.) in benzene (50.0 g.). On stirring the reaction mixture a light orange solution was obtained which was refluxed under the column for an hour at 100–110°. The distillate was withdrawn dropwise at 68°. The temperature of distillate rose to 71° after nearly 5 c.c. of it was collected. At this stage the reaction mixture was allowed to reflux further for an hour. The dropwise withdrawal of the azeotrope was renewed and was continued till the distillate had attained a constant temperature, 80°. The subsequent fractions of distillate were collected separately under a high reflux ratio (1:20).

The ethanol was estimated in the fractions collected other than those distilling at 80° Anal. Calcd. for 2 moles ethanol (per mole of alkoxide) 1.80 g., Found ethanol 1.79 g

* R. C. MEHROTRA, J. Ind. chem. Soc. **30**, 385 (1953).

The reaction mixture was evaporated to dryness and the residue crystallised from benzene. A light orange microcrystalline solid (5.0 g.) was obtained. Anal. Calcd. for $(C_7H_4O_3)_2Ti(OEt)_2$, Ti 17.48%, Found Ti 17.46%.

Molar ratio: 1:2

i) Benzene (57.0 g.), titanium ethoxide (2.98 g.) and salicylic acid (3.60 g.) were refluxed under the column. The alcohol liberated in the reaction was removed completely by fractionation. After nearly 3 c.c. distillate was collected, a finely divided red precipitate began to settle from the reaction mixture. The deep red microcrystalline precipitate was filtered and was washed with ether. A deep red microcrystalline solid (3.14 g.) was obtained after drying at $60^\circ/0.5$ mm.

Anal. Azeotrope: Calcd. for 4 moles of ethanol 2.35 g., Found ethanol 2.18 g.; Calcd. for $Ti(C_7H_5O_3)_2$ Ti 14.99%, Found Ti 14.42%.

ii) Ether (40.0 g.), titanium ethoxide (2.82 g.) and salicylic acid (3.31 g.) were stirred and orange-yellow precipitate thus produced was allowed to stand overnight. The precipitate was filtered and was washed with ether. It was dried at $50^\circ/0.5$ mm. A deep orange solid (3.5 g.) was obtained. Found Ti 14.98%.

Molar ratio: 1:3

Ether (53.0 g.), titanium ethoxide (2.81 g.) and salicylic acid (5.13 g.) were stirred to give an orange finely divided precipitate. It was refluxed for 4 hours. The precipitate was filtered and was washed with ether and was finally dried at $50^\circ/0.5$ mm. A dark orange powder (2.19 g.) was obtained. Anal. Found Ti 14.36%.

The above results indicate, that the above product is largely titanium di-salicylate, which is also formed at room temperature, as in previous experiment, when only 2 moles of acid are present. Hence in temperature range $25-35^\circ$, only di-salicylate is formed even in presence of higher proportion of acid.

Molar ratio: 1:4

A deep red solution was obtained by stirring together titanium ethoxide (2.46 g.), salicylic acid (5.98 g.) and benzene (60.0 g.). It was refluxed at $110-120^\circ$ and the alcohol produced in the reaction was removed. The deep red solid was filtered and washed with ether and was finally dried at $65^\circ/1$ mm. A deep red microcrystalline powder (3.54 g.) was obtained. Anal. Azeotrope: Calcd. for 4 moles ethanol 1.94 g., Found ethanol 1.84 g.; Calcd. for an equimolar mixture of $(C_7H_4O_3)_2Ti$ and $H_2[(C_7H_4O_3)_3Ti]$, Ti 12.34% Found Ti 12.88%.

Reactions between titanium isopropoxide and salicylic acid

Molar ratio: 1:1

Titanium isopropoxide (2.24 g.), salicylic acid (1.12 g.) and benzene (61.0 g.) gave on stirring a light orange solution, which was refluxed under the column at $100-110^\circ$ for an hour. The azeotrope was withdrawn dropwise at 71° . When nearly 2 c.c. were collected the temperature of the distillate rose to 73° ; at this stage it was allowed to reflux further for an hour. The azeotrope was redrawn gradually till it attained constant temperature 80° . Subsequent fractions were collected separately. Isopropanol was estimated in all fractions but pure benzene. Anal. Calcd. for 2 moles isopropanol 0.94 g., Found 0.94 g.

The reaction mixture was concentrated under reduced pressure and the concentrate left for crystallisation. The crystals were dried at 60°/1 mm. Orange red crystals (2.0 g.) were obtained. Anal. Calcd. for $(C_7H_4O_3)Ti(OPr^1)_2$, Ti 15.86% Found Ti 15.88%.

Molar ratio: 1:2

Titanium isopropoxide (2.71 g.), salicylic acid (2.69 g.) and benzene (61.0 g.) were treated as above and the alcohol produced was also removed as before. A deep red microcrystalline solid (3.1 g.) was finally obtained, after washing it with ether and drying it at 65°/0.5 mm. Anal. azeotrope: calcd. for 4 moles isopropanol 2.28 g., Found isopropanol 2.17 g. Calcd. for $Ti(C_7H_4O_3)_2$, Ti 14.99%, Found Ti 14.50%.

Molar ratio: 1:3

Titanium isopropoxide (2.22 g.), salicylic acid (3.23 g.) and benzene (80.0 g.) were refluxed and the alcohol produced in reaction was removed. The deep red solid was filtered and was washed with ether. A dark red microcrystalline powder (2.8 g.) was obtained after drying at 65°/1 mm. Anal. azeotrope: calcd. for 4 moles isopropanol 1.87 g. Found isopropanol 1.79 g.; calcd. for an equimolar mixture of $(C_7H_4O_3)_2Ti$ and $H_2[(C_7H_4O_3)_3Ti]$, Ti 12.34%, Found Ti 12.60%.

Reactions between titanium ethoxide and mandelic acid

Molar ratio: 1:1

i) Titanium ethoxide (1.75 g.), mandelic acid (1.16 g.) and benzene (26.0 g.), on stirring yielded a light yellow solution, which was evaporated to dryness under reduced pressure, after standing overnight. The residue was dried at 60°/0.5 mm. A white (slightly yellow) granular powder (2.3 g.) was obtained. Anal. calcd. for $(C_8H_6O_3)Ti(OEt)_2$, Ti 16.63%, $C_8H_6O_3$ 52.09%, Found: Ti 16.37%, $C_8H_6O_3$ 54.00%.

ii) Titanium ethoxide (3.18 g.), mandelic acid (2.13 g.) and benzene (38.0 g.) were refluxed at 100—110°. The alcohol liberated in the reaction was removed completely. The reaction mixture was evaporated to dryness under reduced pressure. The residue was dried at 60°/0.5 mm. A finely divided yellowish white mass (4.75 g.) was obtained. Anal. azeotrope, calcd. for 2 moles of ethanol 1.25 g., Found: 1.01 g. ethanol. Found: Ti 16.51%, $C_8H_6O_3$ 55.47%.

Reaction between $(C_8H_6O_3)Ti(OEt)_2$ and n-amyl alcohol.

Compound, $(C_8H_6O_3)Ti(OEt)_2$ (1.63 g.), n-amyl alcohol (2.31 g.) and benzene (33.0 g.) gave a deep yellow solution on stirring, which was refluxed at 100° for 2 hrs, after which the alcohol liberated in the reaction was removed azeotropically. The reaction mixture left was evaporated to dryness under reduced pressure. The residue was dried at 85—90° at 0.5 mm. Anal. azeotrope: calcd. for 2 moles (per mole of compound) of ethanol 0.51 g. Found: ethanol 0.47 g.; calcd. for $(C_8H_6O_3)_2Ti(C_5H_{11}O)_2$ Ti 12.87%, Found Ti 13.03%.

Molar ratio: 1:2

i) Mandelic acid (2.40 g.) was added to a solution of titanium ethoxide (1.80 g.) in benzene (10.0 g.). A voluminous white precipitate gradually settles on stirring. The reaction mixture was allowed to stand overnight. Supernatant liquor was decanted off and the remaining solid was dried at 60°/0.5 mm. A white powder (3.03 g.) was obtained.

Anal. Calcd. for $(C_8H_6O_3)_2Ti \cdot \frac{(OEt)}{(C_8H_7O_3)}$, Ti 12.15%, $C_8H_6O_3$ 76.40%, Found: Ti 12.01%, $C_8H_6O_3$ 76.88%.

Above compound (1.70 g.) was heated at 160–165°/1.0 mm. for an hr. A pale yellow residue (1.63 g.) was left behind. Found: Ti 12.46%, $C_8H_6O_3$ 81.25%.

Reactions of $(C_8H_6O_3)_2Ti \cdot \frac{(OEt)}{(C_8H_7O_3)}$

a) With excess mandelic acid: Compound (1.87 g.), mandelic acid (2.30 g.) and benzene (30.0 g.) were refluxed under column for 2 hrs. at 100–110°. The alcohol liberated in the reaction was fractionated out. Reaction product was washed with ether and was dried at 60°/1 mm. A pale yellow powder (1.2 g.) was obtained. Anal.: calcd. for an equimolar mixture of $(C_8H_6O_3)_2Ti$ and $H[(C_8H_6O_3)_3Ti]$, Ti 11.30%, Found Ti 10.70%, Found ethanol 0.176 g. against 0.218 g. (present in compound).

b) With excess tertiary butanol: Compound (0.92 g.), tert. butanol (2.1 g.) and benzene (25.0 g.) were refluxed under the column for an hr. at 100°. The liberated alcohol was fractionated out. The remaining solid was filtered off and was washed with ether, a white powder (0.5 g.) was obtained after drying it at 60°/0.5 mm. Anal.: calcd. for $(C_8H_6O_3)_2Ti \cdot \frac{(OC_4H_9)}{(C_8H_7O_3)}$, Ti 11.35%, Found Ti 11.98%. Anal. azeotrope: calcd. for 1 mole (per mole of compound) ethanol 0.107 g., found: 0.025 g. ethanol.

ii) Titanium ethoxide (2.89 g.), mandelic acid (3.86 g.) and benzene (64.0 g.) were refluxed at 100–110°. The alcohol produced in the reaction was fractionated out. A white solid (4.86 g.) was obtained after washing it with ether and drying at 65°/1.5 mm. Anal.: azeotrope: calcd. for 2.9 moles of ethanol 1.65 g., found ethanol 1.65 g. Found Ti 11.8%, $C_8H_6O_3$ 74.92%.

Molar ratio: 1:3

Titanium ethoxide (2.07 g.), mandelic acid (4.14 g.) and benzene (80.0 g.) were refluxed together, alcohol produced in reaction was removed. The product was washed with ether and dried at 65°/1.5 mm. A pale white solid was obtained (2.51 g.). Anal.: azeotrope; Calcd. for 4 moles ethanol, 1.63 g., found 1.55 g. ethanol. Calcd. for an equimolar mixture of $(C_8H_6O_3)_2Ti$ and $H_2[(C_8H_6O_3)_3Ti]$, Ti 11.30%, $C_8H_6O_3$ 88.70%. Found: Ti 11.29%, $C_8H_6O_3$ 83.80%.

Molar ratio: 1: > 4

A mixture of titanium ethoxide (2.27 g.), mandelic acid (6.92 g.) and benzene (80.0 g.) was treated as above. A finely divided yellowish white powder (2.18 g.) was finally obtained. Anal.: azeotrope: Calcd. for 4 moles ethanol 1.79 g., Found 1.55 g. ethanol, Found: Ti 11.09% $C_8H_6O_3$ 85.50%.

Molar ratio: 1:3

Titanium ethoxide (1.39 g.), mandelic acid (2.81 g.) and ether (52.0 g.) gave a voluminous white precipitate. The reaction mixture was refluxed for 3 hrs. The precipitate was filtered off and was washed with ether. It was dried at 60°/5.0 mm. A white powder (2.1 g.) was obtained. Anal. Calcd. for $(C_8H_6O_3)_2Ti \cdot \frac{(OEt)}{(C_8H_7O_3)}$, Ti 12.15%, $C_8H_6O_3$ 76.40%. Found: Ti 11.69%, $C_8H_6O_3$ 76.89%.

Reactions of titanium isopropoxide and mandelic acid

Molar ratio: 1:1

Mandelic acid (1.74 g.) was admitted to a solution of titanium isopropoxide (3.25 g.) in benzene (30.0 g.). The reaction mixture became warm on stirring and a faintly yellow solution was obtained which was refluxed under the column at 100—110°. Alcohol liberated in the reaction was fractionated out. The remaining solution was evaporated to dryness under reduced pressure. A light yellow powder (3.7 g.) was obtained after drying it at 65°/1 mm. Anal.: azeotrope: Calcd. for 2 moles isopropanol 1.37 g., Found: 1.26 g. isopropanol. Calcd. for $(C_8H_6O_3)_2Ti(OPr^i)_2$, Ti 15.16%, $C_8H_6O_3$ 47.46%, Found Ti 15.02%, $C_8H_6O_3$ 46.43%.

Molar ratio: 1:2

A white finely divided suspension was obtained by stirring mandelic acid (3.61 g.), titanium isopropoxide (3.37 g.) and benzene (40.0 g.), which was refluxed under column at 100—110°. Isopropanol produced in reaction was removed azeotropically. A white powder (3.7 g.) was obtained after washing it with ether and then drying it at 60°/1 mm. Anal.: azeotrope: calcd. for 3 moles isopropanol 2.14 g., Found 1.94 g. isopropanol. Calcd. for: $(C_8H_6O_3)_2Ti \cdot (OPr^i)_2 \cdot (C_8H_7O_3)$, Ti 11.74%, $C_8H_6O_3$ 73.52%, Found: Ti 11.63%, $C_8H_6O_3$ 73.62%.

Above compound, $(C_8H_6O_3)_2Ti \cdot (OPr^i)_2 \cdot (C_8H_7O_3)$, (1.2 g.) was heated for 2 hrs. at 120°/1 mm. No loss in weight was observed. Anal.: Found Ti 11.87%, $C_8H_6O_3$ 73.63%.

$(C_8H_6O_3)_2Ti \cdot (OPr^i)_2 \cdot (C_8H_7O_3)$, (1.53 g.), tertiary butanol (3.60 g.) and benzene (25.0 g.) were refluxed for an hr. at 90°. The isopropanol produced in the reaction was fractionated out. A white powder was obtained after drying at 65°/1 mm. Anal.: azeotrope: Calcd. for 1 mole isopropanol (per mole of compound) 0.225 g., Found isopropanol 0.137 g.; Calcd. for $(C_8H_6O_3)_2Ti \cdot (OC_4H_9)_2 \cdot (C_8H_7O_3)$, Ti 11.35%, Found Ti 11.21%.

Molar ratio: 1:4 (excess)

Titanium isopropoxide (3.32 g.), mandelic acid (7.33 g.) and benzene (81.0 g.) were refluxed for 2 hrs. Isopropanol produced in reaction was fractionated out. A pale yellow powder (4.5 g.) was obtained after being washed with ether and drying at 65°/1 mm. Anal.: azeotrope: Calcd. for 4 moles isopropanol 2.81 g., found isopropanol 2.57 g.; Calcd. for an equimolar mixture of $(C_8H_6O_3)_2Ti$ and $H_2[(C_8H_6O_3)_2Ti]$, Ti 11.30%, $C_8H_6O_3$ 88.70%, found Ti 11.44%, $C_8H_6O_3$ 87.64%.

Reactions of titanium ethoxide and lactic acid

i) A light yellow solution was obtained by stirring titanium ethoxide (2.20 g.), lactic acid (0.94 g.) and benzene (25.0 g.), which was evaporated to dryness under reduced pressure. The residue was dried at 35°/1.5 mm. A light yellow powder (2.2 g.) was obtained. Anal.: Calcd. for $(C_3H_4O_3)Ti(OEt)_2$, Ti 21.19%, Found Ti 21.03%.

ii) Titanium ethoxide (2.75 g.), lactic acid (1.11 g.) and benzene (42.0 g.) were refluxed under column at 90—100°, ethanol produced in reaction was removed azeotropically. The remaining light yellow solution was evaporated to dryness under reduced

pressure. A pale white solid (2.7 g.) was obtained by drying residue at 60°/1 mm. Anal.: Azeotrope: calcd. for 2 moles ethanol 1.09 g., found ethanol 1.10 g.; Found Ti 21.55%.

Molar ratio: 1:2

i) Titanium ethoxide (2.28 g.), lactic acid (1.84 g.) and benzene (30.0 g.) gave white precipitate on stirring. After allowing reaction mixture to stand overnight, supernatant liquor was decanted off. Remaining mass was dried at 35°/1.5 mm. to yield a white powder (2.0 g.). Anal.: Calcd. for $(C_3H_4O_3)_2Ti \cdot (C_3H_5O_3)$, Ti 17.74%, Found Ti 18.21%.

ii) Titanium ethoxide (2.12 g.), lactic acid (1.74 g.) and benzene (41.0 g.) were refluxed at 90—100° under column, ethanol produced in the reaction was fractionated out. Remaining reaction mixture was processed as above. A white powder (2.26 g.) was obtained. Anal.: azeotrope: Calcd. for 4 moles ethanol 1.67 g., found ethanol 1.27 g., found Ti 18.51%.

Above compound (0.825 g.), $(C_3H_4O_3)Ti \cdot (C_3H_5O_3)$, lactic acid (0.28 g.) and benzene (30.0 g.) were refluxed under column at 90—100°, ethanol liberated in reaction was fractionated out. The reaction product was filtered and was washed with ether. A white powder (0.91 g.) was obtained after drying the product at 60°/1.5 mm. Anal.: azeotrope: calcd. for 1 mole ethanol (per mole of compound) 0.137 g., found ethanol 0.116 g.; Calcd. for an equi molar mixture of $(C_3H_4O_3)_2Ti$ and $H_2[Ti(C_3H_4O_3)_3]$, Ti 17.80%, found Ti 18.56%.

Reactions of titanium isopropoxide and lactic acid

Molar ratio: 1:1

i) Titanium isopropoxide (3.26 g.), lactic acid (1.03 g.) and benzene (17.0 g.) were stirred together to yield a clear solution, which was evaporated to dryness under reduced pressure after allowing it to stand overnight. After drying residue at 60°/0.5 mm. a white granular mass (2.99 g.) was obtained. Anal. Calcd. for $(C_3H_4O_3)Ti (OPr^i)_2$, Ti 18.86%, found Ti 18.49%.

ii) Titanium isopropoxide (5.99 g.), lactic acid (1.90 g.) and benzene (50.0 g.) were refluxed under column at 90—100°. Isopropanol produced in reaction was fractionated off. The remaining solution was evaporated to dryness under reduced pressure. After drying the residue a white glistening mass (5.4 g.) was obtained. Anal.: Found Ti 18.78%, Found isopropanol 2.42 g. against 2.53 g. calcd. for 2 moles.

Molar ratio: 1:2

i) On stirring together, titanium isopropoxide (7.42 g.), lactic acid (4.71 g.) and benzene (10.0 g.), a white precipitate is formed and reaction mixture becomes warm. Finally a white powder (6.55 g.) was obtained. Anal.: Calcd. for an equimolar mixture of $(C_3H_4O_3)_2Ti$ and $(C_3H_4O_3)Ti \cdot (OPr^i)$, Ti 18.86%, Found Ti 18.78%.

ii) Titanium isopropoxide (6.24 g.), lactic acid (3.95 g.), and benzene (47.0 g.) were refluxed under column, liberated alcohol was removed azeotropically. The supernatant liquor was decanted off from reaction product and the residue was dried at 60°/0.5 mm. A white powder (5.2 g.) was obtained. Anal.: azeotrope: Calcd. for 4 moles isopropanol 5.27 g., found isopropanol 4.45 g.; found Ti 18.39%.

Molar ratio: 1:4

Titanium isopropoxide (4.04 g.), lactic acid (5.23 g.) and benzene (43.0 g.) were treated as above. A white powder (3.6 g.) was obtained after washing product with ether and drying it at 60°/0.5 mm. Anal.: azeotrope: Calcd. for 4 moles isopropanol 3.41 g., found isopropanol 3.16 g.; calcd. for an equimolar mixture of $(C_3H_4O_3)_2Ti$ and $H_2[(C_3H_4O_3)_3Ti]$, Ti 17.80%, found Ti 18.24%.

Authors would like to thank M/S Peter Spence Ltd., Widnes, Lancashire, U. K., for gift of alkyl titanates. I. D. V. is grateful to Scientific Research Committee, U. P., India, for award of a scholarship.

Lucknow and Gorakhpur (India), Chemical Laboratories, Universities of Lucknow and Gorakhpur.

Bei der Redaktion eingegangen am 22. Juli 1959.