

Derivatives of Aluminium with Some α -Hydroxy Carboxylic Acids

By A. K. RAI, R. K. MEHROTRA and R. C. MEHROTRA

Summary

The reactions of aluminium isopropoxide and aluminium chloride with salicylic, mandelic and lactic acids in different stoichiometric ratios have been studied under absolutely anhydrous conditions. Mandelic and lactic acids were found to give tri-derivatives, whereas the salicylic acid gave only di-salicylate when the ratios of alkoxide and the acid was 1:3 (or slightly higher) or an equimolecular mixture of di- and tri-salicylate when the ratio was increased to 1:3.4 (or 3.4).

The existence of simple tri-acylates had been in doubt for a long time. The synthesis of tri-acetate and higher acylates was described for the first time by MEHROTRA and PANDE¹⁾ and has been since then confirmed by a number of investigators^{2) 3)}.

In view of the above, it was considered of interest to make a detailed study of derivatives of aluminium with substituted carboxylic acids like salicylic lactic and mandelic acids also. BURROWS and WARK⁴⁾ have expected that aluminium compounds would be obtained corresponding to one of the other of the acids, $H[Al(C_7H_4O_3)_2]$ and $H_3[Al(C_7H_4O_3)_3]$, but their attempts to isolate either in a pure condition were unsuccessful. All isolated salts contained sodium (or its equivalent), aluminium and salicylic acid in the ratio 2:1:2, associated with the solvent of crystallisation and could be considered salts of the acid $H_2\left[(C_7H_4O_3)_2Al\left\langle\begin{array}{l} OH \\ OH_2 \end{array}\right.\right]$. They were unsuccessful in introducing the third molecule of salicylic acid or another sodium atom and no compound of the type, $Na_3[Al(C_7H_4O_3)_2]$ or $Na[Al(C_7H_4O_3)_2]$ could be isolated from aluminium hydroxide and salicylic acid or alkali sali-

¹⁾ R. C. MEHROTRA and K. C. PANDE, *J. Inorg. Nucl. Chem.* **2**, 60 (1956); **4**, 128 (1957).

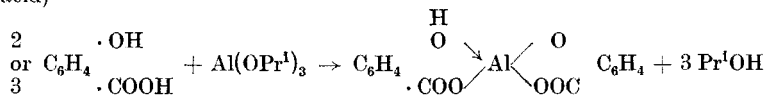
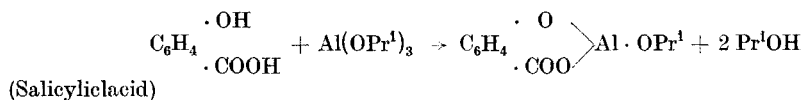
²⁾ A. GILMOUR, A. JOBLING and S. M. NELSON, *J. Chem. Soc.* **386**, 1972 (1956).

³⁾ A. E. LEGER, R. L. HAINES, C. E. HUBLEY, Z. C. HYDE and H. SHEFFER, *Cand. J. Chem.* **35**, 799 (1957).

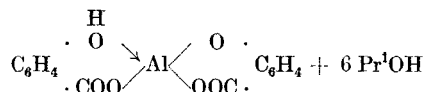
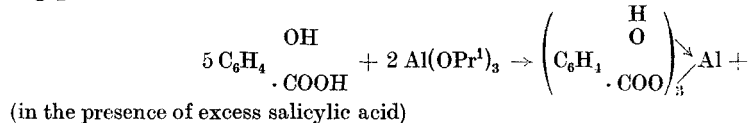
⁴⁾ G. J. BURROWS and I. W. WARK, *J. Chem. Soc.* 222 (1928).

cylates. Recently, BABKO and RYCHKOVA⁵⁾ appear to have found some evidence for the formation of tri-salicylates from their electro-metric studies.

In view of the above conflicting conclusions of a number of investigators, the study was extended to the preparation of the various α -hydroxy acid derivatives of aluminium. The reactions of aluminium isopropoxide and salicylic acid in different molar ratios were studied under absolutely anhydrous conditions. The reaction mixtures were refluxed under a column and the benzene-isopropanol azeotrope was collected slowly under a high reflux ratio. Estimation of the isopropanol liberated and analysis of the products indicated that the reactions can be represented by the following equations:



During these investigations, it was observed that when the ratio of the alkoxide and the acid was 1:3 (or slightly higher) the di-salicylate was the final product. However, when the ratio was increased to 1:3.5 (or >3.5), an equimolecular mixture of di- and tri-salicylate was obtained as the resulting product:

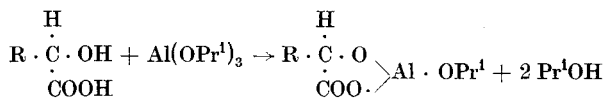


In spite of repeated efforts, the pure tri-salicylate could not be prepared in any case even when variations were made in the mode of the preparation, such as (i) the isopropoxide was added to a large excess of salicylic acid dissolved in ether so that the acid remained throughout in excess or (ii) the above reaction product was allowed to stand at the room temperature for a few hours before being refluxed.

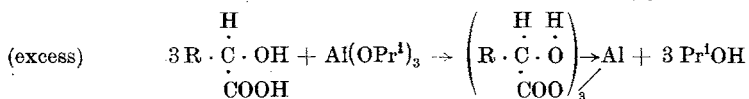
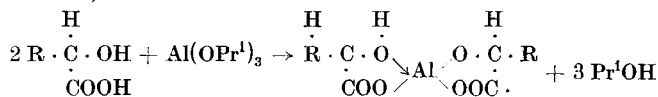
The investigations were further extended to the study of the reactions of aluminium isopropoxide with mandelic and lactic acid. Contrary to the above, trimandelates and tri-lactates of aluminium were successfully synthesised by refluxing the reaction mixtures of aluminium isopropoxide and the corresponding acids in ratio 1:3 under a column when the liberated isopropanol was removed azeotropically with benzene. These reactions were

⁵⁾ H. BABKO and J. N. RYCHKOVA, Zhur. Obschei Khim. J. Gen. Chem. **18**, 1617 (1948).

studied in different molar ratios and were found to proceed as indicated by the following equations:

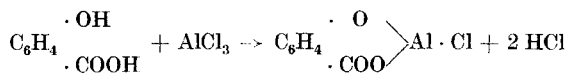


(Lactic or mandelic acid)

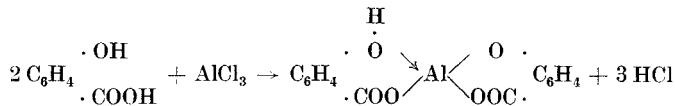


(R = CH₃ or C₆H₅)

The reactions between anhydrous aluminium chloride and hydroxy acids were also carried out in ether and benzene by refluxing the reaction mixtures in different molar ratios. The behaviour of salicylic acid was found to be similar to that described in the case of alkoxides.

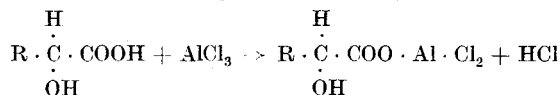


(Salicylic acid)

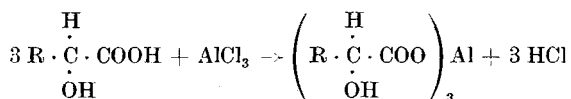
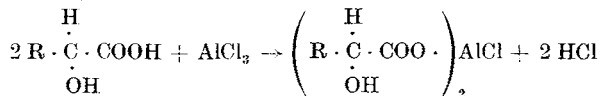


(2 moles or excess)

In the case of mandelic and lactic acids, however, the reactions appeared to follow a slightly different course from that observed in the case of the isopropoxide. It has been found that only one mole of hydrogen chloride is liberated by the reaction between aluminium chloride and the mandelic acid in 1:1 molar ratio. Similarly, the reaction in 1:2 and 1:3 molar ratios, liberates 2 and 3 moles of hydrogen chloride respectively. The reactions can, therefore, be represented by the following equations:



(Lactic or mandelic acid)



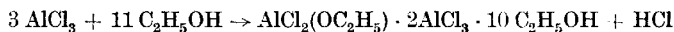
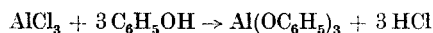
(3 moles or more)

(R = CH₃ or C₆H₅)

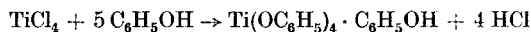
From the reactions of aluminium isopropoxide and zirconium isopropoxide⁶⁾, it appears that the phenolic hydroxy of salicylic acid is more reactive than the alcoholic hydroxy group of the α -hydroxy acid (mandelic or lactic). This results in the formation of aluminium tri-mandelate and zirconium tetra-mandelate, whereas, the corresponding reactions in the case of salicylic acid yield only a mixture of di- and tri-salicylate in the case of aluminium and only a tri-salicylate derivative in the case of zirconium.

However, in the case of titanium⁷⁾, both the salicylic, as well as lactic and mandelic acids give mixture of di- and tri-derivatives when three (or more than three) of the above acids are caused to react with one mole of titanium alkoxide under conditions similar to those employed in the present investigation in the reactions of aluminium alkoxides and fatty acids.

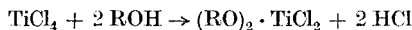
In the case of zirconium and titanium, the alkoxides show reactions which are parallel to those exhibited by the tetrachlorides for both salicylic as well as lactic and mandelic acids. Aluminium isopropoxide and chloride also show similar reactivity towards salicylic acid but their behaviour depict marked difference from each other in the case of mandelic and lactic acids. This can be easily understood as aluminium chloride shows very marked differences in its reactivity towards phenoxy and alkoxy compounds. Thus its reactions with phenol⁸⁾ and ethanol⁹⁾ can be represented by the following equations:



Similar but less marked difference has been observed in the reactivity of titanium tetrachloride with phenol¹⁰⁾ and ethanol¹¹⁾. These reactions can be represented mainly as bellow:



(or more)



(or excess)

⁶⁾ R. N. KAPOOR and R. C. MEHROTRA, J. Amer. Chem. Soc. **82**, 3495 (1960); **80**, 3569 (1958).

⁷⁾ I. D. VERMA and R. C. MEHROTRA, J. prakt. Chem. [10], **4**, 245 (1960).

⁸⁾ H. FUNK and E. ROGLER, Z. anorg. Chem. **252**, 323 (1944).

⁹⁾ H. FUNK, J. SCHORMULLER and W. HENSIGER, Z. anorg. allgem. Chem. **205**, 361 (1932).

¹⁰⁾ H. FUNK and E. ROGLER, Z. anorg. Chem. **252**, 323 (1944).

¹¹⁾ J. S. JENNINGS, W. WARDLAW and W. J. R. WAY, J. Chem. Soc. 637 (1936).

Experimental

All glass apparatus with standard interchangeable joints were used and special precautions were taken to exclude moisture. Aluminium isopropoxide (Judex), redistilled at 106°C/1.5 mm, anhydrous aluminium chloride, salicylic acid, lactic acid and mandelic acid (B. D. H.) were used during the recent investigations. The acids were dried under reduced pressure at 80°C/0.1 mm. Benzene and ether were stored over sodium wire and finally distilled over sodium metal.

Analytical Methods

For aluminium, the compound was ignited directly in the case of salicylate derivatives to aluminium oxide. Aluminium was determined gravimetrically as oxinate in the case of lactate and mandelate derivatives.

The salicylate group in the compounds was estimated by alkaline permanganate method (BOTTGER, "Newer Methods of Volumetric Chemical Analysis", 1938, p. 63).

Mandelate group was determined by the method described by VERMA and PAUL¹²) which consists in oxidation of mandelic acid by excess standard ceric sulphate and back titration of residual ceric sulphate against standard ferrous ammonium sulphate solution.

1. Reactions of Aluminium Isopropoxide and Salicylic Acid

(I) Aluminium isopropoxide and salicylic acid; molar ratio 1:1. a) Salicylic acid (1.7 g, 1 mole) was added to a solution of aluminium isopropoxide (2.54 g., 1 mole) in benzene. The reaction mixture was refluxed and benzeneisopropanol azeotrope was collected during a period of five to six hours. The azeotrope contains 1.50 g. of isopropanol against 1.49 g. required for two moles. The separated product on drying and on analysis was found to contain Al, 11.6; salicylate, 61.2%. Calc. for $\text{Al}(\text{OPr}^i)$ (Salc.): Al, 12.14; Salicylate 61.26%.

b) Salicylic acid (2.68 g., 1 mole) was added to a solution of aluminium isopropoxide (3.97 g., 1 mole) in benzene. A clear solution was obtained from which a white product separated out on refluxing. The product was washed thoroughly with ether, dried at 65°C/1.5 mm and on analysis was found to contain Al, 11.84; Salicylate, 58.62%. Calc. for $\text{Al}(\text{OPr}^i)$ (Salc.): Al, 12.14; Salicylate, 61.26%.

(II) Aluminium isopropoxide and salicylic acid; molar ratio 1:2. A mixture of salicylic acid (2.89 g., 2 moles), aluminium isopropoxide (2.13 g., 1 mole) and benzene was refluxed under a column and the azeotrope was collected between 72–80°C. The azeotrope contains 1.79 g. against 1.87 g. required for three moles of isopropanol. The separated product was washed with ether, dried at 50°C/1.0 mm. and on analysis was found to contain Al, 9.1; Salicylate, 90.2%. Calc. for $\text{Al}(\text{C}_7\text{H}_4\text{O}_3)$ ($\text{C}_7\text{H}_5\text{O}_3$): Al, 8.99; Salicylate, 91.01%.

(III) Aluminium isopropoxide and salicylic acid; molar ratio 1: >3. (a) A clear solution was obtained on mixing aluminium isopropoxide (2.32 g., 1 mole) and salicylic acid (4.71 g., 3 moles) in benzene. On refluxing the reaction mixture, a white product separated out. The product was washed with ether, dried at 60°C/0.5 mm. and was found to contain Al, 8.71; Salicylate, 90.32%. Calc. for $\text{Al}(\text{C}_7\text{H}_5\text{O}_3)$ ($\text{C}_7\text{H}_4\text{O}_3$): Al, 8.99, Salicylate 91.01%.

b) A mixture of aluminium isopropoxide (4.31 g., 1 mole) and salicylic acid (9.24 g., 3.14 moles) in benzene was refluxed under a column and benzene-isopropanol azeotrope was collected which was found to contain 3.65 g. of isopropanol against 3.80 g. required theoretically for three moles. The separated product, after washing with ether and drying at 80°C/0.5 mm., was found to contain Al, 8.81; salicylate, 88.86%. Calc. for $\text{Al}(\text{C}_7\text{H}_5\text{O}_3)$ ($\text{C}_7\text{H}_4\text{O}_3$): Al, 8.99; Salicylate, 91.01%.

¹²) M. R. VERMA and S. D. PAUL, J. Sci. Industr. Res. (India) 13B, 347 (1954).

c) Salicylic acid (7.07 g., 3.44 moles) was added to a benzene solution of aluminium isopropoxide and the reaction mixture was refluxed under a column. The benzene-isopropanol azeotrope was collected during the refluxing of then hours. The azeotrope contained 2.64 g. of isopropanol against 2.69 g. required theoretically for three moles. The product was washed with ether, dried at 60°C/0.5 mm. and on analysis was found to contain Al, 7.49; Salicylate 88.73%. Calc. for equimolecular mixture of $\text{Al}(\text{C}_7\text{H}_5\text{O}_3)_3$ and $\text{Al}(\text{C}_7\text{H}_5\text{O}_3)(\text{C}_7\text{H}_4\text{O}_3)$: Al, 7.30; Salicylate, 92.70%.

d) A solution of salicylic acid (8.80 g., 4.4 moles) in ether was refluxed in a bath and a solution of aluminium isopropoxide (2.95 g., 1 mole) in ether was added drop by drop. A white precipitate separated out slowly. It was washed thoroughly with ether and dried at 55°C/1.0 mm. The product was found to contain Al, 7.35; Salicylate, 88.88%. Calc. for a equimolecular mixture of $\text{Al}(\text{C}_7\text{H}_5\text{O}_3)_3$ and $\text{Al}(\text{C}_7\text{H}_5\text{O}_3)(\text{C}_7\text{H}_4\text{O}_3)$: Al, 7.30; Salicylate, 92.70%.

IV. Aluminium tertiary butoxide and salicylic acid; molar ratio 1:3. A mixture of salicylic acid (5.27 g., 3 moles) and aluminium tertiary butoxide (3.13 g., 1 mole) in benzene was refluxed for a few hours. A white product separated out. It was filtered out, washed with ether and dried at 65°C/1.5 mm. On analysis, it was found to contain: Al, 8.64; Salicylate, 88.73%. Calc. for $\text{Al}(\text{C}_7\text{H}_4\text{O}_3)(\text{C}_7\text{H}_5\text{O}_3)_3$: Al, 8.99, Salicylate, 91.01%.

2. Reactions of Aluminium Chloride and Salicylic Acid

(I) Aluminium Chloride and Salicylic acid; molar ratio 1:1. Salicylic acid (1.63 g., 1 mole) was added to a solution of aluminium chloride (1.57 g., 1 mole) in ether. The reaction mixture was refluxed for 8–9 hours, till the evolution of hydrogen chloride ceased. The volatile fraction was distilled out and the compound was dried at 60°C/1.0 mm. A white powder was obtained which on analysis was found to contain Al, 13.40; Cl, 16.90; Salicylate, 67.7%. Calc. for $\text{AlCl}(\text{sal.})$: Al, 13.59; Cl, 17.86; Salicylate, 68.55%.

(II) Aluminium chloride and Salicylic acid; molar ratio 1:2. A mixture of solutions of salicylic acid (2.83 g., 2 moles) and aluminium chloride (1.36 g., 1 mole) in ether was refluxed for 16–17 hours till the evolution of hydrogen chloride ceased. A white product separated out which after washing with ether and drying at 60°C/1.5 mm. was found to contain Al, 8.60; Salicylate, 88.50%. Calc. for $\text{Al}(\text{C}_7\text{H}_4\text{O}_3)(\text{C}_7\text{H}_5\text{O}_3)_2$: Al, 8.99, Salicylate, 91.01%.

(III) Aluminium chloride and salicylic acid; molar ratio 1:3. A solution of salicylic acid (5.68 g., 5.5 moles) in ether was added to a solution of aluminium chloride (1.57 g., 1 mole) in ether. A vigorous reaction was observed with the evolution of heat and hydrogen chloride gas. The evolution of hydrogen chloride gas ceased after about twenty hours of refluxing. The separated product was washed thoroughly with ether and dried at 60°C/1.5 mm. On analysis it was found to contain Al, 9.3; Salicylate, 90.4%. Calc. for $\text{Al}(\text{C}_7\text{H}_4\text{O}_3)(\text{C}_7\text{H}_5\text{O}_3)_3$: Al, 8.99; Salicylate, 91.01%.

3. Reactions of Aluminium Isopropoxide and Mandelic Acid

(I) Aluminium isopropoxide and mandelic acid; molar ratio 1:1. Aluminium isopropoxide (5.86 g., 1 mole) was mixed with mandelic acid (4.37 g., 1 mole) in benzene and the reaction mixture was refluxed under a column. The benzene isopropanol azeotrope was collected in about ten hours which was found to contain 3.21 g. of isopropanol against 3.44 g. required theoretically. The separated product was dried and on analysis was found to contain Al, 10.82; mandelate, 61.02%. Calc. for $\text{Al}(\text{OPr}^i)(\text{mand.})$: Al, 11.42; mandelate, 63.56%.

(II) Aluminium isopropoxide and mandelic acid; molar ratio 1:2. Aluminium isopropoxide (2.0 g., 1 mole) and mandelic acid (2.98 g., 2 moles) were suspended in benzene. The reaction mixture was refluxed and the benzene isopropanol azeotrope was collected in

about twelve hours of refluxing. The azeotrope was found to contain 1.70 g. of isopropanol against 1.76 g. required for three moles. The separated product was washed thoroughly with ether and dried at 60°C/0.5 mm. It was found to contain Al, 8.40, mandelate, 90.10%. Calc. for Al(C₈H₆O₃) (C₈H₇O₃): Al, 8.23; mandelate, 91.77%.

(III) Aluminium isopropoxide and mandelic acid; molar ratio 1:3. Mandelic acid (5.50 g., 3 moles) was added to a solution of aluminium isopropoxide (2.46 g., 1 mole) in benzene. The reaction mixture was refluxed for about twelve hours under a column and the azeotrope was slowly collected which was found to contain 2.13 g. of isopropanol against 2.17 g. required theoretically. The separated product was washed with ether and dried at 50°C/0.5 mm. It was found to contain Al, 5.76; mandelate, 93.40%. Calc. for Al (mand)₃: Al, 5.61; mandelate, 94.39%.

4. Reactions of Aluminium Chloride and Mandelic Acid

(I) Aluminium chloride and mandelic acid, molar ratio 1:1. A solution of mandelic acid (1.35 g., 1 mole) in ether was added to a solution of aluminium chloride (1.16 g., 1 mole) in ether. The reaction mixture was shaken vigorously and refluxed for about six hours. The supernatant liquid was decanted off after allowing it to stand overnight and was dried at 60°C/0.5 mm. It was found to contain Al, 10.60; Cl, 27.70; mandelate, 61.90%. Calc. for AlCl₂ (mand): Al, 10.86, Cl, 28.47; mandelate, 60.67%.

(II) Aluminium chloride and mandelic acid, molar ratio 1:2. Mandelic acid (1.39 g., 2 moles) was dissolved in ether and added to a solution of aluminium chloride (0.61 g., 1 mole) in ether. The reaction mixture was refluxed for about eight hours and the supernatant liquid was decanted off. The product was dried at 60°C/0.5 mm. and was found to contain Al, 7.90; Cl, 9.20; mandelate, 83.10%. Calc. for AlCl (mand)₂: Al, 7.39; Cl, 9.72; mandelate, 82.88%.

(III) Aluminium chloride and mandelic acid; molar ratio 1: > 3. a) A white precipitate was obtained immediately on mixing a solution of mandelic acid (3.04 g., 3.46 moles) to a solution of aluminium chloride (0.77 g., 1 mole) in ether. The mixture was allowed to stand for about seventy hours, filtered, washed with ether and dried at 50°C/1.5 mm. The product on analysis was found to contain Al, 7.9, Cl, 9.2, mandelate, 81.8%. Calc. for AlCl (mand)₂: Al, 7.39; Cl, 9.72, mandelate, 82.88%.

b) A solution of mandelic acid (2.52 g., 3.71 moles) in ether was added to a solution of aluminium chloride (0.62 g., 1 mole). The reaction mixture was refluxed with some benzene for about fifty hours till the evolution of hydrogen chloride ceased. The separated product was washed, dried at 60°C/1.5 mm. and on analysis was found to contain Al, 5.99, mandelate 92.05%. Calc. for Al (mand)₃: Al, 5.61; mandelate, 94.38%.

5. Reactions of Aluminium Isopropoxide and Lactic Acid

(I) Aluminium isopropoxide and lactic acid, molar ratio 1:1. Aluminium isopropoxide (3.24 g., 1 mole), lactic acid (1.43 g., 1 mole) and benzene were mixed together and the reaction mixture was refluxed for about four hours under a column. The azeotrope was collected which was found to contain 1.82 g. of isopropanol against 1.90 g. required for two moles. The separated product was washed with ether and dried at 60°C/1.0 mm. The product on analysis was found to contain Al, 15.90%. Calc. for Al(OPr) (lact): Al, 15.48%.

(II) Aluminium isopropoxide and lactic acid, molar ratio 1:2. A little heat was evolved with the formation of gelatinous suspension on adding lactic acid (3.27 g., 2 moles) to a benzene solution of aluminium isopropoxide (3.71 g., 1 mole). The reaction mixture was refluxed under a column and the azeotrope was collected which was found to contain 3.00 g.

of iso-propanol against 3.02 g. required theoretically for three moles. The separated product was washed thoroughly with ether, dried at 60°C/1.5 mm. and was found to contain: Al, 12.80%; Calc. for $\text{Al}(\text{C}_3\text{H}_7\text{O}_2)_3$ ($\text{C}_3\text{H}_5\text{O}_2$): Al, 13.21%.

(III) Aluminium isopropoxide and lactic acid; molar ratio 1:3. a) A mixture of lactic acid (3.10 g., 3 moles), aluminium isopropoxide (2.36 g., 1 mole) in benzene was refluxed under a column. The benzene-isopropanol azeotrope was slowly collected and found to contain 1.92 g. of isopropanol against 2.08 g. required for three moles. The separated product was washed thoroughly with ether and dried at 70°C/1.0 mm. The product on analysis was found to contain Al, 9.02%. Calc. for $\text{Al}(\text{lact})_3$: Al, 9.18%.

b) A gelatinous suspension was obtained on mixing lactic acid (3.52 g., 3 moles) and aluminium isopropoxide (2.66 g., 1 mole) in benzene. The reaction mixture was allowed to stand for a few days. The product was filtered, washed thoroughly with ether and dried at 70°C/1.0 mm. The product on analysis was found to contain Al, 9.35%. Calc. for $\text{Al}(\text{lact})_3$: Al, 9.18%.

6. Reactions of Aluminium Chloride and Lactic Acid

(I) Aluminium chloride and lactic acid; molar ratio 1:1. A solution of lactic acid (0.98 g., 1 mole) in ether was added to a solution of aluminium chloride (1.45 g., 1 mole) in ether. A white precipitate was obtained. The reaction mixture was refluxed for six hours and the separated product was washed with ether. The product after drying at 60°C/1.0 mm. was found to contain Al, 14.00; Cl, 36.2%. Calc. for $\text{AlCl}_2(\text{lact})$: Al, 14.38; Cl, 37.93%.

(II) Aluminium chloride and lactic acid; molar ratio 1:2. Solutions of aluminium chloride (1.97 g., 1 mole) and lactic acid (2.60 g., 2 moles) in ether were mixed together. A white precipitate was obtained instantaneously. The reaction mixture was refluxed for five hours and washed with ether. The white powder obtained on drying at 60°C/1.0 mm. was found to contain Al, 11.20; Cl, 13.90%. Calc. for $\text{AlCl}(\text{lact})_2$: Al, 11.12; Cl, 14.60%.

(III) Aluminium Chloride and lactic acid, molar ratio 1:3. A solution of lactic acid (4.10 g., 3.85 moles) in ether was mixed to a solution of aluminium chloride (1.58 g., 1 mole) in ether. A white precipitate was obtained. The reaction mixture was refluxed for nearly sixty hours with some benzene. The separated product was washed thoroughly with ether, dried at 60°C/1.0 mm. and on analysis was found to contain Al, 9.33%. Calc. for $\text{Al}(\text{lact})_3$: Al, 9.18%.

Gorakhpur (India), Chemical Laboratories, University of Gorakhpur.

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