

Cation exchange in case of silica sesquioxide gels is always greater than that calculated from the law of mixture, the maximum difference being observed in the case of magnesium saturated gel. This shows that exchange of bases in soils is mainly regulated by the presence of silica. As a matter of fact the amount of exchangeable Na in one g. of pure silica gel is the same as that in 1 g. of silica-alumina mixed gel containing only 0.44 g. of silica. It is also remarkable that whereas the amount of exchangeable metal ion from pure ferric hydroxide is small compared with silica, mixed gels of ferric oxide and silica yield more metal ions than pure silica itself. This indicates a great increase in the degree of dispersion of silica gel when precipitated with ferric hydroxide. Such is also the case with $\text{SiO}_2/\text{Al}_2\text{O}_3$ mixtures. Fig. 1a and b show the relation between the composition of gels and exchangeable cation. It may be noted here that the amounts of exchangeable ions in these artificial gels are of the same order of magnitude as are noticed in the clay fractions of soils.

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A Note on the Constitution of the Reduction Product of Trichloromethylparaconic Acid.

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The reduction of trichloromethylparaconic acid (I) has been studied by Fittig and Miller (*Ber.*, 1887, 20, 3181; *Annalen*, 1889, 255, 43) and Meyers (*J. Amer. Chem. Soc.*, 1902, 24, 525). They assign the formula (II) to the reduction product.

While studying the condensation of chloral with various acids, the present authors had occasion to prepare trichloromethylparaconic acid and reduce it. As a result of their work they consider the reduction product is a dibasic acid as represented in formula (III) and has not the structure (II) given by Fittig and Miller. This has been proved (a) by preparing from the reduction product diesters (IV and IVa),

anhydride (V), diacid chloride (VI), dianilide (VII) and di-*p*-toluidide (VIII), (b) by reducing the ethyl ester (IX) and anilide (X) of trichloroparaconic acid to produce respectively the acid ester (XI) and acid anilide (XII) which give the diester (IV) and dianilide (VII), and (c) by preparing tricarballic acid (XIII) by the action of concentrated sulphuric acid which converts the CH_2CHCl_2 group to CH_2COOH group (Meldrum and Vaidyanathan, *Proc. Indian Acad. Sci.*, 1935, 1, 510).

EXPERIMENTAL.

Butane- δ , δ -dichloro- $\alpha\beta$ dicarboxylic acid (III), the reduction product under discussion, was prepared according to Fittig and Miller (*loc. cit.*), (Found: Equiv., 107.6. Calc. for dibasic acid, 107.5).

The methyl ester (IVa) is a colourless oil. b. p. $135^\circ/11$ mm. (Found: Cl, 29.0. $\text{C}_8\text{H}_{12}\text{O}_4\text{Cl}_2$ requires Cl, 29.2 per cent).

The ethyl ester (IV) is a sweet smelling oil, b. p. $215^\circ/50$ mm. (Found: Cl, 26.7. $\text{C}_{10}\text{H}_{16}\text{O}_4\text{Cl}_2$ requires Cl, 26.9 per cent).

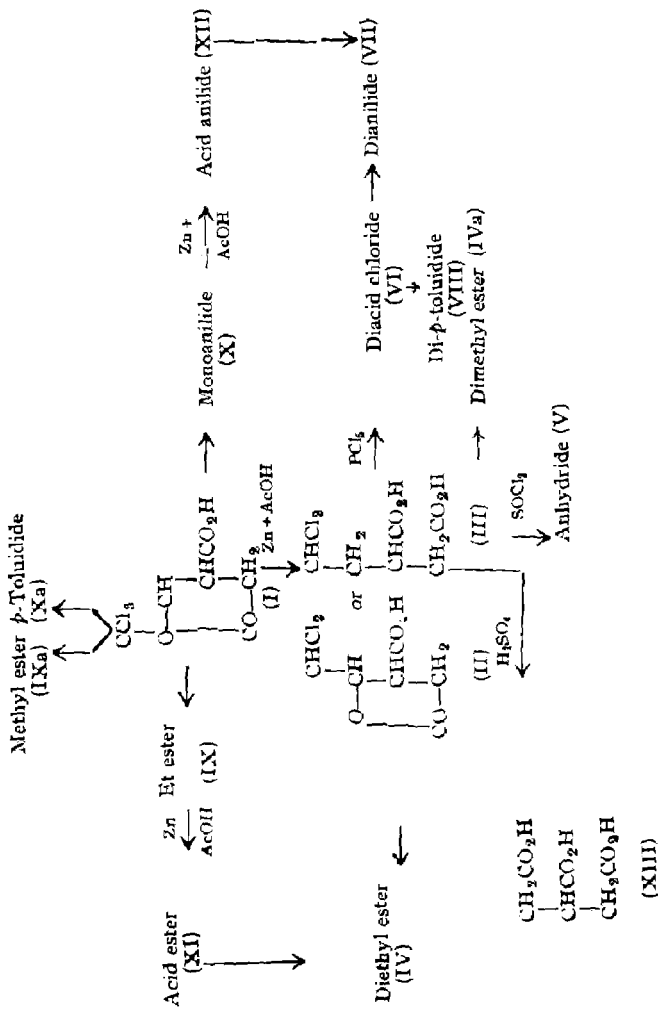
The anhydride (V).—The product (III) (5g.) was treated with thionyl chloride (7g.) at 65° for 4 hours and the excess of thionyl chloride was removed at 95° . The residue after being dried on a porous plate was crystallised from petroleum ether in shining plates, m. p. $76^\circ-77^\circ$. (Found: Cl, 36.1. $\text{C}_6\text{H}_6\text{O}_3\text{Cl}_2$ requires Cl, 36.0 per cent).

The crude acid chloride (VI) was obtained by heating the reduction product (5g.) with PCl_5 (10g.) and after cooling pouring into petroleum ether, the precipitated anhydride was removed and the residue distilled, b. p. $123^\circ/5$ mm.

The anilide (VII), obtained from the acid chloride (VI) in petrol ether, crystallised from dilute acetic acid in needles, m. p. $176^\circ-77^\circ$. (Found: Cl, 19.4. $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2\text{Cl}_2$ requires Cl, 19.7 per cent).

The p-toluidide (VIII) crystallised from dilute acetic acid, m. p. $209^\circ-10^\circ$. (Found: Cl, 18.0. $\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}_2\text{Cl}_2$ requires Cl, 18.0 per cent).

Tricarballic acid (XIII).—The reduction product (III) (10g.) was treated with concentrated sulphuric acid (20 c.c., 95 %) at 100° for 3 hours and the liquid poured on ice and neutralised with lead carbonate. The filtrate was twice extracted with ether to remove unchanged reduction product and the aqueous solution concentrated, filtered and cooled. The resulting precipitate was crystallised from hot water, m. p. 165° ,



(recorded 165°). The *anhydride* melts at 132° - 34° (recorded 132°) and the *anilide* melts at 262° - 64° (recorded 252°).

Derivatives of Trichloromethylparaconic acid (I).

The *methyl ester* (IXa) crystallised from methyl alcohol, m.p. 77° . (Found: Cl, 40.7. $C_7H_7O_4Cl_3$ requires Cl, 40.7 per cent).

The *ethyl ester* (IX) is a colourless sweet smelling oil, b.p. $173^{\circ}/10$ mm. (Found: Cl, 38.5. $C_8H_9O_4Cl_3$ requires Cl, 38.6 per cent).

The *anilide* (X) crystallised from dilute acetic acid in light shining plates, m.p. 165° - 66° . (Found: Cl, 32.7. $C_{12}H_{10}O_3NCl_3$ requires Cl, 33.0 per cent).

The *p-toluidide* (Xa) crystallised from dilute alcohol in thin white plates, m.p. 173° - 74° . (Found: Cl, 31.8. $C_{13}H_{12}O_3NCl_3$ requires Cl, 31.6 per cent).

The *ethyl hydrogen ester* (XI).—(IX) was reduced with zinc and acetic acid as usual, b.p. $190^{\circ}/20$ mm. (Found: Cl, 29.0. $C_8H_{12}O_4Cl_2$ requires Cl, 29.2 per cent).

The *acid anilide* (XII), obtained by the reduction of (X) with zinc and acetic acid, crystallised from chloroform, m.p. 121° - 22° . (Found: Cl, 24.7. Equiv., 289.2. $C_{12}H_{13}O_3NCl_2$ requires Cl, 24.4 per cent. Equiv., 290.1).