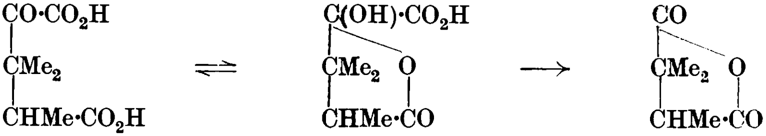
LXXVIII.—*Ring-chain Tautomerism. Part XV. The Hydroxy-lactone Type.*

By EUGENE ROTHSTEIN and CHARLES WILLIAM SHOPPEE.

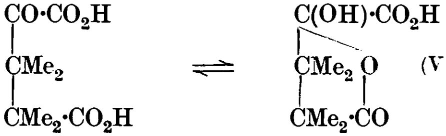
IN Part I of this series (Kon, Stevenson, and Thorpe, J., 1922, **121**, 654; see also Rothstein, Stevenson, and Thorpe, J., 1925, **127**, 1073), it was shown that the acid $C_8H_{12}O_5$ (Balbiano's acid) is a mixture of two tautomeric individuals (I and II). The evidence for the presence of the tautomeride (II) consisted in the fact that on treatment with *o*-phenylenediamine in acetic acid solution an acidic addition product, which was not a salt, was formed, and on heating this, or on boiling the two substances together, the usual quinoxaline derivative was formed. There was additional evidence for the existence of the hydroxy-lactone isomeride (II), inasmuch as the latter gave off carbon monoxide, with the formation of trimethylsuccinic anhydride (III), when heated above its melting point (*loc. cit.*).



(I.) (II.) (III.)

The authors have now investigated the methyl derivative (IV) of Balbiano's acid (Francis and Willsdon, J., 1913, **103**, 2238), because it seemed to them that the presence of the second *gem*-dimethyl group should stabilise the hydroxy-lactonic form (V) of the acid. This has been found to be the case.

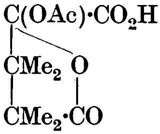
(IV.)



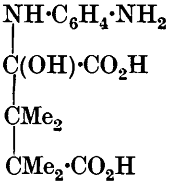
(V.)

When the acid (V) was titrated with baryta solution, it behaved as a monobasic acid. When it was boiled with *N*/100-baryta, the hydroxy-lactone ring underwent fission to the extent of about 40%. Similar treatment with *N*/10-baryta increased the fission to 95%, but complete fission could not be obtained. Balbiano's acid, under similar conditions, always yielded the normal barium salt (of the dibasic acid). The above figures were also obtained after the acid (V) had been esterified to the dimethyl ester and then regenerated by hydrolysis.

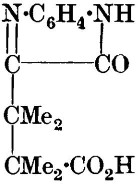
Another striking difference between the acid (V) and Balbiano's acid, indicating the difference in stability of the respective hydroxy-lactonic rings, is that the former yielded an *acetyl* derivative (VI) on treatment with acetic anhydride. This derivative decomposes sodium hydrogen carbonate and behaves as a monobasic acid on titration.



(VI.)



(VII.)



(VIII.)

Like Balbiano's acid, the compound (V) gives an *addition product* (VII) with *o*-phenylenediamine, and also the *condensation product*

(VIII). There is, however, an important distinction between the two compounds. Whereas the condensation product can be obtained from Balbiano's acid by boiling the acid itself with *o*-phenylenediamine, the only methods by which the corresponding derivative is formed from the tetramethyl acid are by heating the addition product, by fusing the acid and the phenylenediamine together, and by fusing the dimethyl ester with the same compound.

It is evident, therefore, that the hydroxy-lactone phase is the stable form of the tetramethyl compound, and, unlike Balbiano's acid, in solution this is not a tautomeric mixture of (IV) and (V). The presence of alkalis or acids, however, tends to shift the equilibrium in favour of the ketonic form.

It is therefore now possible to record the existence of three members of an homologous series, differing from one another in the possession of an additional methyl group, in which the influence of this group on the carbon tetrahedral angle is clearly demonstrated by the chemical and physical properties of the substances described. The ββ-dimethyl compound is static as a hydrated ketone, the ββγ-trimethyl acid (I and II) is a tautomeric mixture of the ketonic and the hydroxy-lactonic form, whilst, finally, the ββγγ-tetramethyl acid (V) is static as the hydroxy-lactone.

EXPERIMENTAL.

Hydroxy-lactone of α-Keto-ββγγ-tetramethylglutaric acid (V).—The acid was prepared from bromohydroxyphorone by the method of Francis and Willsdon (*loc. cit.*). After recrystallisation from toluene, or ethyl acetate and light petroleum, it melted at 140° (Found: C, 53·2; H, 6·9. Calc.: C, 53·4; H, 6·9%).

Titration with $N/100$-baryta solution gave M, 202, 204 [Calc.: M (monobasic), 202]. When the acid was boiled with $N/100$- and with $N/10$-baryta solution, and then titrated with $N/20$-hydrochloric acid, the values of M were 162 and 107, respectively. Balbiano's acid, both on direct and on back titration, gave the value M, 95 [Calc.: M (dibasic), 94].

When the acid was heated above its melting point, it yielded carbon monoxide (11·9 litres per g.-mol.), and tetramethylsuccinic anhydride was found in the residue.

The dimethyl ester, b. p. 170°/15 mm., was prepared by the action of methyl iodide on the disilver salt, or by Phelp and Tillotson's alcohol-vapour method. It crystallised from benzene, or from chloroform and ligroin, in plates, m. p. 103°. The ester could not be characterised by the formation of ketonic derivatives.

Acetyl Derivative of the Acid $C_9H_{14}O_5$ (VI).—The acid (V) was heated under reflux with acetic anhydride for one hour, and the excess of the latter was then removed in a vacuum desiccator containing potash. The product, twice crystallised from benzene and petroleum, formed stellate clusters of needles, m. p. 149° (Found : C, 54·0; H, 6·5; *M*, 241. $C_{11}H_{16}O_6$ requires C, 54·1; H, 6·6%; *M*, monobasic, 244).

Addition Product with o-*Phenylenediamine* (VII).—The acid (V) (0·5 g.), dissolved in the minimum of water, was treated with 10% excess of *o*-phenylenediamine, dissolved in glacial acetic acid. On warming and rubbing, a pale buff precipitate appeared, which separated from alcohol in plates, m. p. 160° (Found : C, 58·7; H, 7·1; N, 8·8. $C_{15}H_{22}O_5N_2$ requires C, 58·4; H, 7·1; N, 9·0%).

The substance decomposes sodium hydrogen carbonate, but not sodium hydroxide solution. When heated above its melting point, it loses water and yields the condensation product (VIII).

Condensation Product with o-*Phenylenediamine* (VIII).—(*a*) The acid (V) (0·5 g.) and *o*-phenylenediamine (0·3 g.) were fused together at 165° for ½ hour. After cooling, the product was treated with a small quantity of boiling alcohol; the almost colourless residue crystallised from acetic acid in tiny cubes, m. p. 238—239°. The alcoholic filtrate slowly deposited the addition compound as a buff precipitate.

(*b*) The dimethyl ester (0·4 g.) and *o*-phenylenediamine, similarly heated together, gave the same product.

The substance, after being crystallised twice from acetic acid, melted at 240° (Found : C, 64·9; H, 6·4. $C_{15}H_{18}O_3N_2$ requires C, 65·6; H, 6·6%). It was reprecipitated unchanged from sodium hydroxide solution by hydrochloric acid, and did not decompose sodium hydrogen carbonate. Like the corresponding condensation product of Balbiano's acid, it turned blue litmus violet-red.

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