CLXXIII.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part IX. The Effect of the* spirocyclo*Pentane Grouping on the Five-carbon Intra-annular Tautomeric Nucleus.*

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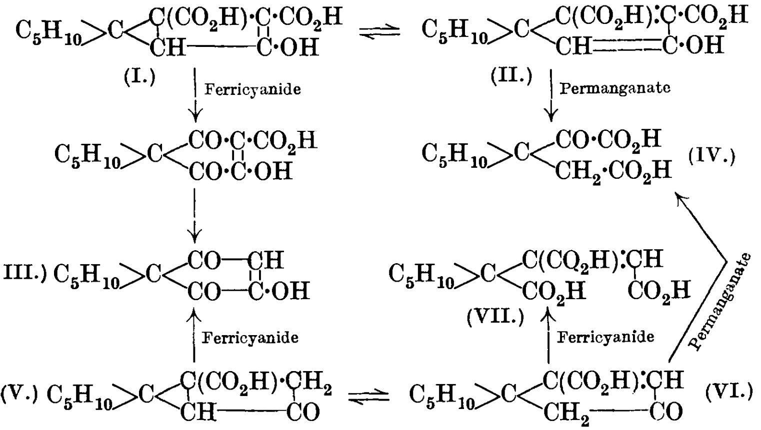
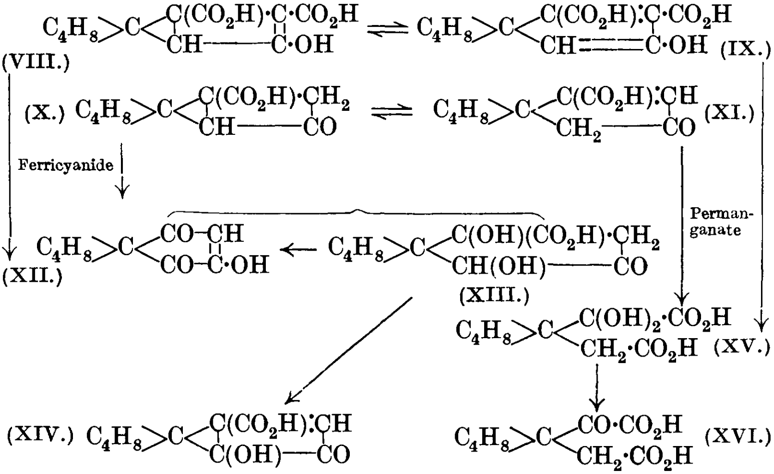
EXPERIMENTS on the oxidation by alkaline ferricyanide of the cyclohexane*spirodicyclo*pentene acid (I, II) carried out by Ingold, Seeley, and Thorpe (J., 1923, **123**, 853) resulted in the production of a cyclic 1 : 4-diketone (III). The quinonoid character of this compound anticipated on the basis of the semi-aromatic character of the type of system discussed in these communications was substantiated by Hassell and Ingold (J., 1926, 1836), who showed that its monoxime is also a nitroso-compound having a close similarity to *p*-nitrosophenol. Whereas the formation of the diketone (III) is attributed to form (I) of the parent acid, oxidation with permanganate yielded as main product an α-ketoglutaric acid (IV) evidently derived from form (II) only. The monobasic ketonic acids (V, VI) showed stronger evidence of the monocyclic phase. Not only did permanganate give the ketoglutaric acid (IV), but ferricyanide yielded, in addition to the 1 : 4-diketone (III), a substituted aconitic acid (VII) obviously derived from form (VI).



The relationship between these results and those obtained in the *gem*-dimethyl series has already been discussed (Ingold, Seeley, and Thorpe, *loc. cit.*) and the object of this paper is to place on record the results which have been obtained in a similar investigation of the corresponding acids of the *cyclo*pentane*spirodicyclo*pentene series.



The dibasic acid (VIII, IX) (Ingold, Lanfear, and Thorpe, J., 1923, **123**, 3140) closely resembles its *cyclo*hexane analogue in yielding with ferricyanide only a cyclic 1 : 4-diketone (XII) and with permanganate only oxalic acid and a substituted αα-dihydroxyglutaric acid (XV), which on dehydration gives an α-ketoglutaric acid (XVI) analogous to that obtained in the investigation already summarised. The chief divergence in behaviour of the *cyclo*pentane compounds emerged during the study of the monobasic ketonic acid (X, XI). This acid, like its *cyclo*hexane analogue, yielded a 1 : 4-diketone (XII) on oxidation with ferricyanide, but the by-product was not an aconitic acid (indeed no such acid has been encountered in the course of these experiments), but a monobasic hydroxyketonic acid (XIV), which may be assumed to have been formed by elimination of water from the dihydroxyketonic acid (XIII), a probable intermediate in the production of (XII).

Potassium permanganate gave a mixture of the αα-dihydroxyglutaric acid (XV) and the corresponding ketoglutaric acid (XVI). It is thus evident that the unsaturated phase (XI) is certainly present, but since substituted aconitic acids have been shown to be the normal products of oxidation with ferricyanide of forms analogous to (XI) in the cases hitherto examined, the non-appearance of an aconitic acid in this series is remarkable, and suggests that the importance of the unsaturated phase is less in this series than in the *cyclo*hexane series. This conclusion is consistent with the relative order which has been established for the effects of the *gem*-dimethyl group and the *spirocyclo*pentane and *spirocyclo*hexane rings on the basis of other investigations (Becker and Thorpe, J., 1920, **117**, 1579; Lanfear and Thorpe, J., 1923, **123**, 1683; Ingold, Lanfear, and Thorpe, *ibid.*, p. 3140).

EXPERIMENTAL.

(A) *Oxidation of* 5-cyclo*Pentane*spirodicyclo*pentan*-3-*one*-1-*carboxylic Acid* (5-cyclo*Pentane*spirocyclo*penten*-3-*one*-1-*carboxylic Acid*) (X, XI) *with Potassium Ferricyanide.*—The monobasic acid (10 g.) was added to a solution of 200 g. of potassium ferricyanide and 48 g. of potassium carbonate in 800 c.c. of water, which was kept for 168 hours at 60°, then cooled, acidified with hydrochloric acid, and extracted with ether. The solid product obtained from the ether was separated into two fractions (4·2 g., m. p. 140°; 0·25 g., m. p. 85—95°) by crystallisation from ether. The larger fraction was treated with methyl alcohol and sulphuric acid, and the product separated into three fractions by crystallisation from ether. The first fraction, forming the bulk of the material, consisted of nearly pure 3-*methoxy*-5-cyclo*pentane*spirocyclo*penten*-1 : 4-*dione*, which crystallised in needles, m. p. 65° (Found: C, 66·9; H, 6·6. $C_{10}H_{12}O_3$ requires C, 66·6; H, 6·7%). This was reconverted into 5-cyclo*pentane*spirocyclo*penten*-3-*ol*-1 : 4-*dione* (XII) by boiling for

2 hours with hydrochloric acid; the dione was obtained as a yellow, crystalline precipitate on cooling, which crystallised from xylene or water in needles, m. p. 154° (Found: C, 65·4; H, 5·8. $C_9H_{10}O_3$ requires C, 65·0; H, 6·1%). This compound gives a cherry-red colour with alcoholic ferric chloride, liberates carbon dioxide from sodium bicarbonate solution, and discharges the colour of alkaline permanganate. The second fraction of the esterification product, consisting of *methyl* 5-cyclo*pentane*spirodicyclo*pentan*(or cyclo*penten*)-4-*ol*-3-*one*-1-*carboxylate*, crystallised in needles, m. p. 145° (Found: C, 62·7; H, 6·9. $C_{11}H_{14}O_4$ requires C, 62·8; H, 6·7%). The third fraction, which did not solidify, gave the same figures for carbon and hydrogen content on microcombustion as a liquid product obtained by converting the smaller fraction of the original oxidation product into its methyl ester. The two liquids, therefore, were mixed and on distillation in a good vacuum were separated into two fractions, (*a*) b. p. 145°/1 mm. and (*b*) b. p. 165°/1 mm. Fraction (*a*) on hydrolysis with hydrochloric acid gave a product which, after recrystallisation from xylene, had m. p. 154° and was identical with the dione (XII). Fraction (*b*) on acid hydrolysis gave 5-cyclo*pentane*spirodicyclo*pentan*-4-*ol*-3-*one*-1-*carboxylic acid* (5-cyclo*pentane*spirocyclo*penten*-4-*ol*-3-*one*-1-*carboxylic acid*, XIV), which crystallised from xylene in needles, m. p. 110° (decomp.) (Found: C, 61·2; H, 5·9. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·2%).

(B) *Oxidation of* 5-cyclo*Pentane*spirodicyclo*penten*-3-*ol*-1 : 2-*dicarboxylic Acid* (5-cyclo*Pentane*spirocyclo*pentadien*-3-*ol*-1 : 2-*dicarboxylic Acid*) (VIII, IX) *with Potassium Ferricyanide.*—A solution of the dibasic acid (1 g.), potassium ferricyanide (20 g.), and potassium carbonate (20 g.) in 80 c.c. of water was kept for 256 hours at 60°. The cooled product was acidified with hydrochloric acid, and ether then extracted a substance which solidified on prolonged desiccation; after recrystallisation from xylene, this had m. p. 154° and was identical with the dione (XII) described above. No other substances could be detected.

(C) *Oxidation of* 5-cyclo*Pentane*spirodicyclo*pentan*-3-*one*-1-*carboxylic Acid* (5-cyclo*Pentane*spirocyclo*penten*-3-*one*-1-*carboxylic Acid*) (X, XI) *with Alkaline Permanganate.*—To a solution of the monobasic acid (3 g.) and potassium carbonate (2 g.) in 50 c.c. of water, 1000 c.c. of 1% potassium permanganate solution (equiv. to 5O) were slowly added. After 12 hours, the excess of permanganate was destroyed by sulphur dioxide and the precipitated manganese oxides were filtered off and extracted with hot water. The combined filtrate and aqueous extract was partly evaporated, slightly acidified with hydrochloric acid, made just alkaline with ammonia, and treated with calcium chloride; no oxalate was precipitated, The acidified liquid was extracted with ether, yielding 1·5 g. of *αα-dihydroxy*cyclo*pentane*-1 : 1-*diacetic acid* (XV), which crystallised from chloroform in prisms, m. p. 98° (Found : C, 49·7; H, 6·7. $C_9H_{14}O_6$ requires C, 49·6; H, 6·5%). This compound was converted by heating at 90° for an hour into α-keto*cyclo*pentane-1 : 1-diacetic acid (XVI), m. p. 112° after crystallisation from ligroin (compare Lanfear and Thorpe, J., 1923, **123**, 1688) (Found : C, 54·3; H, 5·7. Calc. : C, 54·0; H, 6·0%); which was converted by heating with *o*-phenylenediamine in glacial acetic acid into the quinoxaline, m. p. 222°, described by Lanfear and Thorpe (*loc. cit.*) (Found : C, 66·3; H, 6·0. Calc. : C, 66·1; H, 5·9%).

(D) *Oxidation of* 5-cyclo*Pentane*spirodicyclo*penten*-3-*ol*-1 : 2-*dicarboxylic Acid* (5-cyclo*Pentane*spirocyclo*pentadien*-3-*ol*-1 : 2-*dicarboxylic Acid*) (VIII, IX) *with Alkaline Permanganate*.—To a solution of the dibasic acid (1 g.) and potassium carbonate (0·7 g.) in 50 c.c. of water, 65 c.c. of 3% potassium permanganate solution (equiv. to 4O) were slowly added. After 12 hours, the excess of permanganate was destroyed by sulphur dioxide, and the alkaline solution obtained as in the case of the monobasic acid was freed from oxalate as calcium salt (0·6 g.). The acidified filtrate on extraction with ether yielded 1·2 g. of a mixture, m. p. 96—105°, of the keto- and dihydroxy-acids (XV, XVI), consisting mainly of the former (Found : C, 52·7; H, 6·3%). This mixture was converted into the quinoxaline, m. p. 222°, mentioned above.

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