

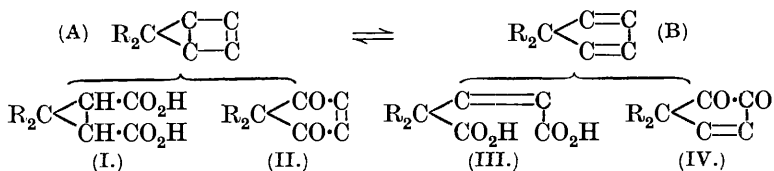
CCXLIII.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part VII. Tautomerism Corresponding with that of Nitrosophenol and Quinoneoxime in the bicycloPentane Series.*

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THE experiments here described originated in the discovery (Ingold, Seeley, and Thorpe, J., 1923, **123**, 853) of the close analogies between

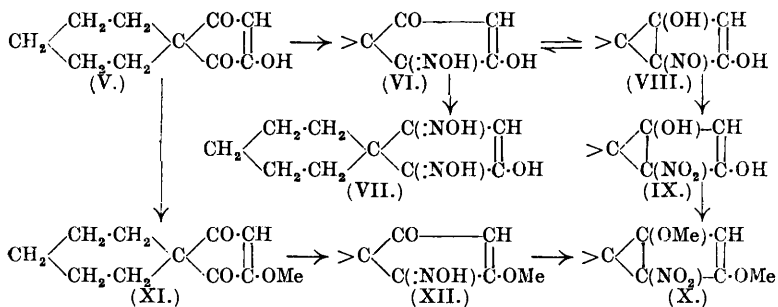
certain compounds of the *gem*-dialkylbicyclopentene series and the corresponding derivatives of benzene.

By the oxidative degradation of bicyclopentene derivatives (J., 1920, **117**, 1362; 1922, **121**, 128; 1923, **123**, 864, 3303) four types of product have been obtained, the formation of two of which (I and III) discloses the tautomeric character of the nucleus (A, B), whilst the other two (II and IV) recall the oxidation of benzene derivatives to *o*- and *p*-quinones :



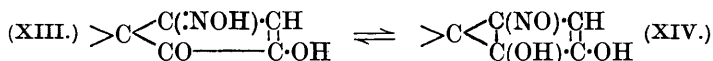
An aromatic characteristic which it was thought might reappear in the five-ring series is that illustrated by the tautomerism of *p*-nitrosophenol with quinoneoxime, and accordingly it was decided to investigate the behaviour towards hydroxylamine of a substance of type (II).

The most available substance of this class was the *cyclohexane-spiro*-compound (V), which was found to react fairly readily with hydroxylamine, forming a *monoxime* (VI), which was convertible, although with difficulty, into the *dioxime* (VII). The oxime also showed evidence of the nitroso-constitution (VIII), since it could readily be oxidised to the *nitro*-compound (IX). The nitro-compound on methylation gave the same *dimethoxynitro*-derivative (X) as was obtained by oxidation and subsequent methylation of the *oxime* (XII) of the methoxy-derivative (XI). These reactions, which are closely parallel to those of quinonemonoxime, are summarised in the following table :



No special proof is offered that the monoxime represented as (VI) and (VIII) has not actually the constitutions (XIII) and (XIV), but we regard preferential oximation in the position

required to produce these structures as intrinsically unlikely,* and the formulæ themselves as less in accord with the properties of the substance than those given above. In any case, the argument respecting the analogy with benzene derivatives is independent of this possible ambiguity.

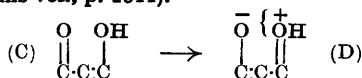


The chemical evidence of the tautomerism of quinoneoxime and *p*-nitrosophenol is of four principal kinds: (a) its formation from quinone by oximation, (b) its conversion into the static dioxime, (c) its formation from phenol by nitrosation, (d) its conversion into *p*-nitrophenol. Of these four lines of evidence, three are paralleled by the present work.

EXPERIMENTAL.

*cyclo*Hexanone was converted into α' -dicyanocyclohexane-1:1-diacetamide by Guareschi's method (*Atti R. Accad. Sci. Torino*, 1900—1901, **36**, 443) and the free acid, prepared by hydrolysis of the imide with sulphuric acid, was purified by extracting it from the carbonaceous residue with acetone and crystallising it from that solvent, this being a more convenient method for the preparation of large quantities than the customary process involving the use of ether. The yield of the imide was 80% and that of the acid 68%. The acid was dibrominated as described by Beesley, Ingold, and Thorpe (*J.*, 1915, **107**, 1080), and the neutral bromoester (yield 80%) converted into ethyl sodio-5-*cyclohexanespiro*-0:1:2-*bicyclopenten*-3-ol-1:2:4-tricarboxylate (Ingold and Thorpe, *J.*, 1919, **115**, 320) (average yield, 22.5%). This was then hydrolysed to a mixture of 5-*cyclohexanespiro*-0:1:2-*bicyclopenten*-3-ol-1:2-dicarboxylic acid and 5-*cyclohexanespiro*-0:1:2-*bicyclopentan*-3-one-1-carboxylic acid in such a way as to produce as large a yield as possible of the former (*loc. cit.*, p. 362). The monocarboxylic acid could not be converted into an oximino-derivative by means of nitrosyl chloride (compare Farmer, Ingold, and Thorpe, *J.*, 1922, **121**, 147). The dibasic acid was oxidised in lots of not more than 10 g. with ferricyanide, as described by Ingold, Seeley, and Thorpe (*loc. cit.*). The difficulty of extracting the product in the presence of the mass of semi-colloidal hydroferrocyanic acid which was also obtained on acidification of the solution was partly

* In structure (C) the OH should be more acidic and the CO less ketonic than usual owing to partial transformation into the betaine (D) (compare Ingold and Ingold, *this vol.*, p. 1311).



avoided by filtering on pulped paper and extracting the filtrate and the gel separately. The yield of 5-cyclohexanespirocyclopenten-3-ol-1 : 4-dione obtained after crystallisation from water and ether-ligroin was 15%.

4-Oximino-5-cyclohexanespirocyclopenten-3-ol-1-one or 4-Nitroso-5-cyclohexanespiro-0 : 1 : 2-bicyclopentene-1 : 3-diol (VI, VIII).—As the condensation did not proceed smoothly in aqueous solution, the ketone in hot pyridine was treated with hydroxylamine hydrochloride (2 mols.). On addition of water, an oil separated which became green and partly solid. The product was extracted with ether, and the extract washed with dilute sulphuric acid, dried, and evaporated. The solid residue was drained from adhering oil and worked up with the aid of ether and ligroin, and the more soluble fractions were combined and crystallised alternately from acetone and ethyl acetate until the m. p. rose to, and remained constant at, 205° (Found : C, 61.2; H, 6.9. $C_{10}H_{13}O_3N$ requires C, 61.5; H, 6.7%). The oxime forms colourless needles, readily soluble in organic solvents, and in alcoholic solution gives a bright cherry-red coloration with ferric chloride. It behaves as a monobasic acid on titration. Prolonged treatment with hydroxylamine in pyridine solution converts it into the dioxime mentioned below. Alkaline ferricyanide oxidises it to the corresponding nitrodiol.

1 : 4-Dioximino-5-cyclohexanespirocyclopenten-3-ol (VII).—This compound can be isolated in small quantity from the sparingly soluble fractions obtained in the preparation of the monoxime, and is also formed by the more prolonged treatment of the monoxime with hydroxylamine in pyridine solution. In all cases, however, the reaction appears to be incomplete and a certain amount of monoxime can be recovered together with coloured by-products. The dioxime separates from ethyl acetate in pale yellow needles which darken at about 240° and decompose at 250° (Found : C, 57.4; H, 6.9. $C_{10}H_{14}O_3N$ requires C, 57.1; H, 6.7%).

4-Nitro-5-cyclohexanespiro-0 : 1 : 2-bicyclopentene-1 : 3-diol (IX).—The monoxime dissolved in acetone was treated with an aqueous solution of potassium ferricyanide (1.5 mols.) and potassium carbonate (1.5 mols.) for 5 days at 30—40°, and the solution acidified with hydrochloric acid and extracted with ether. The product obtained on evaporating the extract was taken up in a small amount of dry ether, and the filtered solution evaporated. After desiccation over sulphuric acid for several days, the solid product was crystallised from acetone-ligroin; long, pale yellow needles, m. p. 137—139°, were then obtained (Found : C, 57.0; H, 6.4. $C_{10}H_{13}O_4N$ requires C, 56.9; H, 6.1%). This compound gives a red-brown colour with ferric chloride and dissolves in sodium

carbonate solution with effervescence, forming a red solution. From the dark red solution in cold concentrated aqueous potassium hydroxide, crimson needles, evidently the *potassium* salt, separate.

3. *Methoxy-5-cyclohexanespirocyclopentene-1 : 4-dione*.—A solution of the hydroxydione in methyl alcohol (4 parts by wt.) was mixed with cold concentrated sulphuric acid ($\frac{1}{3}$ vol.). After 12 hours, the product was poured into water, and the precipitate collected. It was triturated with aqueous sodium hydrogen carbonate; the undissolved portion crystallised from methyl alcohol in stout prisms, m. p. 117° (Found : C, 68.1; H, 7.3. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.2%). This compound gives no colour with ferric chloride and is insoluble in alkali. On boiling with mineral acid, the hydroxydiketone is regenerated.

3. *Methoxy-4-oximino-5-cyclohexanespirocyclopentene-1 : 4-dione* (XII) was obtained along with less soluble products, from which it could not be completely separated, by treating the methoxydiketone with hydroxylamine hydrochloride (2 mols.) in pyridine solution. The product precipitated on pouring the mixture into water was extracted with ether and freed from pyridine by washing with dilute acid. The substance obtained after several crystallisations from ethyl acetate and acetone had m. p. $150-160^{\circ}$, and was contaminated with a less soluble substance (possibly the dioxime) some of which was carried down with all fractions (Found : N, 7.2. $C_{11}H_{15}O_3N$ requires 6.7%). As the available material was insufficient for complete separation, it was oxidised without further purification.

4. *Nitro-1 : 3-dimethoxy-5-cyclohexane-0 : 1 : 2-spirobicyclopentene* (X).—The methoxy-oximino-compound was oxidised at $30-40^{\circ}$ for one week with potassium ferricyanide (2 mols.) and potassium carbonate (2 mols.) in aqueous acetone, and the product extracted with ether after acidification. The residue obtained on evaporation of the extract was redissolved in a little dry ether, and, after filtration, recovered by evaporation. It was completely soluble in aqueous sodium hydroxide, giving an orange-red solution, which, on being shaken with one drop of methyl sulphate, precipitated an oily solid; this, on being worked up with ligroin and ether, yielded pale yellow prisms, m. p. $70-73^{\circ}$. The same product was obtained by direct methylation of the nitrodiol with methyl sulphate and alkali, the product being crystallised in this instance from ligroin-ethyl acetate (Found : C, 59.9; H, 7.1. $C_{12}H_{17}O_4N$ requires C, 60.3; H, 7.1%).

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