

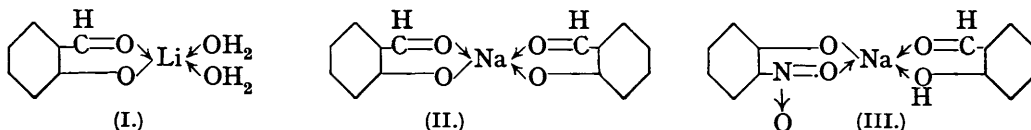
207. The Co-ordination Compounds of Oximes. Part III. Compounds of 4-isoNitroso-1-phenyl-3-methyl-5-pyrazolone with the Alkali Metals, Nickel, and Thallium.

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SIDGWICK and PLANT (J., 1925, **127**, 209) first called attention to the existence of co-ordinated compounds of the alkali metals, describing lithium, sodium, and potassium compounds of ψ -indoxylspirocyclopentane of the general formula $C_{12}H_{12}ONM, C_{12}H_{13}ON$, where M is the alkali metal. These compounds were formulated as containing a quadricovalent metallic atom. The sodium and the potassium compound could be crystallised from toluene, but the lithium compound decomposed during attempts to crystallise it. All the compounds were at once decomposed by water, re-forming the indoxyl compound.

Later, Sidgwick and Brewer (*ibid.*, p. 2379) described a number of compounds of sodium, lithium, and potassium, which, on account of their physical properties, they suggest contain quadricovalent metallic atoms.

Typical of their compounds are lithium salicylaldehyde hydrate (I), sodium disalicylaldehyde (II) (compare Hantzsch, *Ber.*, 1906, **39**, 3089), and sodium *o*-nitrophenolsalicylaldehyde (III).



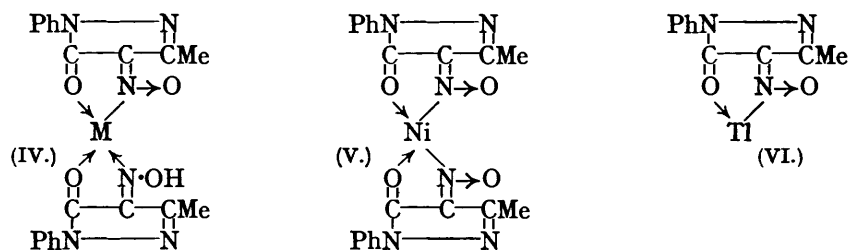
Brewer (J., 1931, 361) extended these observations to rubidium and caesium compounds of salicylaldehyde.

In the last two papers, compounds containing sexacovalent sodium, potassium, rubidium, and caesium were also described. None of these compounds is particularly stable; they are readily decomposed by water or, in the case of such compounds as (I), lose water on heating.

We have now found that 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone (Knorr, *Annalen*, 1887, **238**, 185) forms a series of much more stable quadricovalent, orange-coloured compounds with the alkali metals of the general formula (IV; M = Li, Na, K, Rb, or Cs).

These compounds are practically insoluble in water, but when boiled with it suffer partial decomposition, and isonitrosophenylmethylpyrazolone separates from the solution on cooling. They are soluble in dilute solutions of the corresponding metal hydroxides,

forming, probably, the normal oxime salts; with the exception of the potassium compound, they are readily soluble in solutions of the corresponding carbonates and all are soluble in aqueous sodium carbonate or ammonia.



The solubility in organic solvents varies considerably. The *lithium* and the *sodium* compound are readily soluble in boiling absolute alcohol, the *cæsium* compound less readily, and the *potassium* and the *rubidium* compound very sparingly; the lithium and the *cæsium* compound are moderately soluble in boiling xylene, but the others very sparingly so; all are very slightly soluble in chloroform and benzene, but dissolve fairly readily in boiling *cyclohexanol*. They dissolve in boiling nitrobenzene to very dark solutions and, on cooling, dark-coloured compounds separate in which possibly nitrobenzene partly replaces one of the oxime molecules, for, when washed with ether, the products regain their orange colour but then contain excess of alkali metal.

*iso*Nitrosophenylmethylpyrazolone also forms compounds with nickel and thallium to which structures (V) and (VI) may be assigned, as both are probably co-ordinated: the *nickel* compound is sparingly soluble in organic solvents, but the *thallium* derivative is readily soluble in absolute alcohol and moderately readily in chloroform.

EXPERIMENTAL.

Compounds have been analysed both as prepared and after crystallisation, to ensure that no change such as elimination of *isonitroso*-pyrazolone had occurred during the latter process (compare Hantzsch, *loc. cit.*). The compound which separates in the preparation appears to be, if anything, purer than that obtained by recrystallisation.

Lithium.—4-*iso*Nitroso-1-phenyl-3-methyl-5-pyrazolone (4 g.) was dissolved in hot absolute alcohol (20 c.c.), and lithium hydroxide (0.25 g.), dissolved in the minimum amount of water and diluted with absolute alcohol (10 c.c.), added. After some hours *lithium di-4-isonitroso-1-phenyl-3-methyl-5-pyrazolone* separated in matted hair-like crystals and was washed with a little absolute alcohol and dried over sodium hydroxide; m. p. 203° (decomp.) (Found: C, 58.5; H, 4.2. $C_{20}H_{17}O_4N_4Li$ requires C, 58.7; H, 4.2; Li, 1.7%; *M*, 412). Crystallised from xylene, washed with light petroleum, and dried in a vacuum over sodium hydroxide, it formed an orange-yellow microcrystalline powder, m. p. 196–197° (decomp.) (Found: C, 58.2; H, 4.3; Li, 1.3%; *M*, in camphor, 443).

Sodium.—The pyrazolone (3.5 g.) in boiling absolute alcohol (20 c.c.) was mixed with a solution of sodium (0.18 g.) in absolute alcohol (5 c.c.). *Sodium di-4-isonitroso-1-phenyl-3-methyl-5-pyrazolone* soon crystallised in orange, matted, hair-like masses and was washed with absolute alcohol and dry ether; m. p. 230° (decomp.) (Found: C, 55.6; H, 3.9; N, 19.4; Na, 5.4. $C_{20}H_{17}O_4N_4Na$ requires C, 56.0; H, 4.0; N, 19.6; Na, 5.4%).

The compound separated from *cyclohexanol* as an orange jelly, which was pressed between porous tiles to remove as much as possible of the solvent and then washed with dry ether; the orange amorphous substance obtained was apparently not so pure as the original compound; m. p. indefinite 210–230° (Found: C, 54.5; H, 4.0; Na, 4.9%).

Potassium.—When an alcoholic solution of potassium hydroxide (0.6 g.) was mixed with the pyrazolone (5 g.) in alcohol (30 c.c.), *potassium di-4-isonitroso-1-phenyl-3-methyl-5-pyrazolone* separated rapidly as an amorphous orange powder, which was washed with alcohol; m. p. 248° (decomp.) (Found: C, 53.4; H, 3.9; K, 8.8. $C_{20}H_{17}O_4N_4K$ requires C, 53.8; H, 3.8; K, 8.8%). It separated from *cyclohexanol* as an orange jelly, which was treated in the same way as the sodium compound; m. p. 237° (decomp.) (Found: C, 53.8; H, 4.1; K, 8.7%).

Rubidium.—When a solution of the pyrazolone (2 g.) in absolute alcohol was mixed with

rubidium carbonate (0.6 g.) dissolved in the minimum of water, *rubidium di-4-isonitroso-1-phenyl-3-methyl-5-pyrazolone* separated as an amorphous orange powder, which was washed with alcohol; m. p. 233° (decomp.) (Found: C, 49.8; H, 3.7; Rb, 17.3. $C_{20}H_{17}O_4N_6Rb$ requires C, 49.0; H, 3.4; Rb, 17.4%).

Cæsium.—From a mixture of an absolute alcoholic solution of the pyrazolone (2.5 g. in 20 c.c.) and concentrated aqueous cæsium carbonate (1 g. in 3 c.c.), *cæsium di-4-isonitroso-1-phenyl-3-methyl-5-pyrazolone* separated as an orange jelly-like material, which was pressed between porous tiles, washed with absolute alcohol, and dried in a vacuum over sodium hydroxide; m. p. 204—205° (decomp.) (Found: C, 45.5; H, 3.4; Cs, 23.9. $C_{20}H_{17}O_4N_6Cs$ requires C, 44.7; H, 3.2; Cs, 24.7%). It separated from absolute alcohol as a jelly, which was freed from mother-liquor between porous tiles and dried as before; m. p. 209° (decomp.) (Found: C, 45.0; H, 3.3; Cs, 24.3%). The compound separated from xylene in a similar condition (Found: C, 43.9; H, 3.3; Cs, 23.1%).

Thallium.—The pyrazolone (1 g.) was dissolved in 2*N*-sodium hydroxide (3 c.c.), diluted with water (10 c.c.), and mixed with an aqueous solution of thallos acetate (1.4 g. in 10 c.c.). The orange precipitate was washed with water and dried over sodium hydroxide. *Thallium 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone* crystallised from chloroform, in which it was sparingly soluble, or from absolute alcohol in silky needles; m. p. 219° (decomp.) (Found: C, 29.8; H, 2.0; N, 10.4. $C_{10}H_8O_2N_3Tl$ requires C, 29.6; H, 2.0; N, 10.3%).

Nickel.—A concentrated solution of nickel acetate was added to an alcoholic solution of the pyrazolone, and the precipitate purified by repeated extraction with alcohol; *nickel 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone* was obtained as an olive-green amorphous powder (Found: C, 51.6; H, 3.6; Ni, 12.5. $C_{20}H_{16}O_4N_6Ni$ requires C, 51.9; H, 3.5; Ni, 12.6%). The compound is very slightly soluble in benzene, chloroform, and methyl and ethyl alcohol.

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