

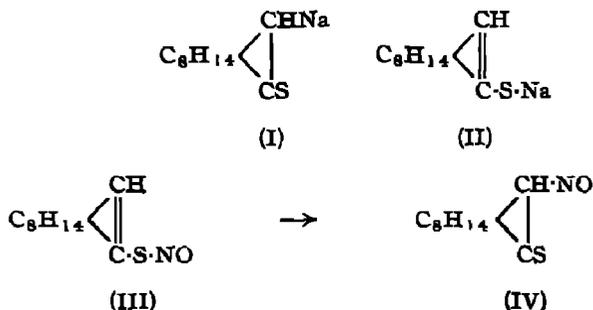
STUDIES IN THE CAMPHOR SERIES. PART V. SOME DERIVATIVES OF ISONITROTHIOPCAMPHOR.

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The formation of *isonitrosothiocamphor* on the basis of its reacting in the thiolic phase takes place by a rearrangement involving the migration of the nitroso group from S to C. *isoNitrosothiocamphor* can give rise to three optical isomers (*d*, *l* and *dl*), each of which in turn should give rise to two geometrical isomers

In a previous communication (Sen, *J. Indian Chem. Soc.*, 1935, 12, 752) it has been suggested that the formation of *isonitrosothiocamphor* (IV, VIII, IX) from *isoamyl nitrite* and *sodio thiocamphor* takes place through C-sodio derivative of thiocamphor (I). But subsequent observations have shown that *sodiothiocamphor* always reacts in the thiolic phase (II) (Sen, *Science & Culture*, 1938, 4, 135).

The formation of *isonitrosothiocamphor* according to this assumption takes place by a rearrangement involving the migration of the nitroso group from sulphur to carbon :



The action of hydroxylamine hydrochloride on *dl-isonitrosothiocamphor* in presence of either sodium hydroxide, or sodium acetate or pyridine gives rise to three compounds, (1) α -camphorquinone dioxime, m.p. 201°, (2) β -camphorquinone dioxime, m.p. 248° and (3) bornylene 1:2:5-thiodiazole, m.p. 218°. The formation of the thiodiazole (V) evidently takes place through the agency of sulphuretted hydrogen which is formed at the first stage of the reaction. The structure has been confirmed by its direct formation from β -camphorquinone dioxime and sulphuretted hydrogen.

latter gave β -camphorquinone dioxime, m.p. 248° as one of the products on treatment with hydroxylamine (cf. Lapworth, *J. Chem. Soc.*, 1907, 91, 1134).

FIG. 1.

dl-isoNitroso in EtOH (1 g. in 100,000 c.c.).

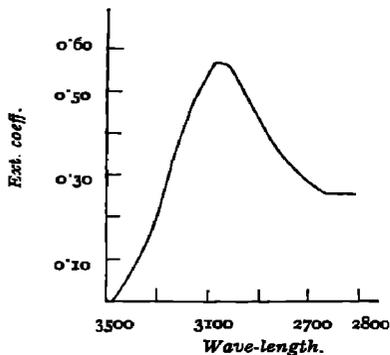


FIG. 2.

l-isoNitroso in EtOH (1 g. in 100,000 c.c.).

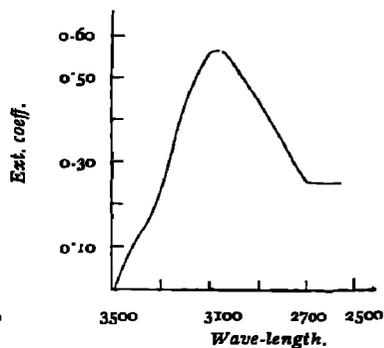


FIG. 3.

l-isoNitroso in EtOH (1 g. in 50 c.c.).

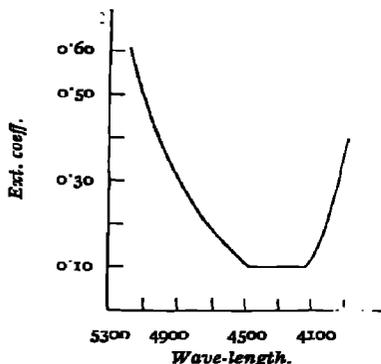
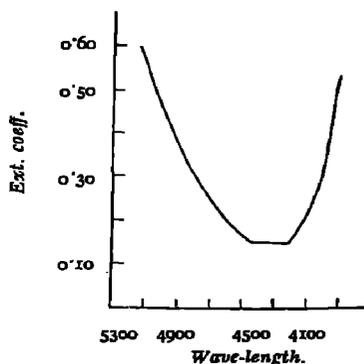


FIG. 4.

dl-isoNitroso in EtOH (1 g. in 50 c.c.).



l-isoNitrosothiocamphor shows dimorphism and dichroism, unlike its *dl*-isomer. In the solid state *l*-isomnitrosothiocamphor is pink, but dissolves in organic solvents with a blue colour. The blue alcoholic solution, if rapidly cooled, gives prismatic crystals, whereas on slow cooling the octahedral form is obtained. The *dl*-isomer is blue both in the solid state and in solution.

The colour of the two isomers during crystallisation from different

solvents under different conditions remained unchanged, and their preparation under identical experimental conditions excludes the possibility of any structural difference. The difference in certain physical properties between isomers of optically active substances is too wellknown. Such difference in colour in optically active isomeride is not very common and deserves mention in this connection. The structural identity of the two isomers in solution has been established by their absorption spectra. Absorption spectra of the two substances at different dilutions show that though there are slight differences in the values of the extinction coefficients, the nature of the curves is the same in both cases (*vide* Figs. 1-4).

EXPERIMENTAL.

Action of Hydroxylamine Hydrochloride on isoNitrosothiocamphor.—*l-iso*Nitrosothiocamphor (10 g.) was dissolved in pyridine (50 c.c.) and heated with hydroxylamine hydrochloride (5 g.) on the water-bath. In a few minutes the blue solution became colourless. The product on being poured into water (500 c.c.) gave a white precipitate, which crystallised from hot alcohol and was identified by mixed m. p. as β -camphorquinone dioxime. (Found: N, 14.22. Calc. for $C_{10}H_{16}O_2N_2$: N, 14.29 per cent). The filtrate from the above on concentration gave α -bornylene 1:2:5-thiodiazole as white needles, m.p. 221°, readily soluble in ether and benzene. (Found: C, 61.93; H, 7.43; S, 16.39. $C_{10}H_{14}N_2S$ requires C, 61.85; H, 7.22; S, 16.49 per cent). $[\alpha]_D^{24} = +75.27$, in 0.31% alcoholic solution. The mother liquor on further concentration gave α -camphorquinone dioxime, m.p. 201° (mixed m.p. remaining undepressed). (Found: N, 14.28. Calc. for $C_{10}H_{16}O_2N_2$: N, 14.29 per cent). Identical products were also obtained in alcoholic solution with hydroxylamine liberated from its hydrochloride by sodium hydroxide or acetate.

*dl-iso*Nitrosothiocamphor on similar treatment gave a mixture of α - and β -camphorquinone dioximes and bornylene-*dl*-1:2:5-thiodiazole, m.p. 218°. (Found: S, 16.42. $C_{10}H_{14}N_2S$ requires S, 16.49 per cent).

The same thiodiazole was also prepared by the action of sulphuretted hydrogen on β -camphorquinone dioxime. β -Camphorquinone dioxime (10 g.) was dissolved in alcohol (100 c. c.) and treated with a saturated solution of sodium acetate (10 g.). Sulphuretted hydrogen was passed through the mixture for 5 hours. The solution was poured into water (500 c. c.) and the separated solid fractionally crystallised from alcohol in white needles, m. p. 218°. The compound was found to be remarkably stable towards potassium permanganate both in acid and alkaline solutions in the cold, but was reduced by zinc and acetic acid to bornylene diamine.

Reduction of Bornylene-1:2:5-thiodiazole.—The above thiodiazole (5 g.), glacial acetic acid (25 c. c.) and zinc dust (5 g.) were heated on a water-bath for 2 hours and filtered. The filtrate after dilution with water (100 c. c.) was made alkaline with dilute sodium hydroxide. The solution was extracted with ether. The extract was dried over anhydrous sodium sulphate and the ether evaporated. The residual brown viscous liquid on treatment with a few c. c. of fuming hydrochloric acid gave bornylene diamine hydrochloride which crystallised from alcohol as white shiny needles, m. p. 287-88°. (Found: C, 50.35; H, 8.5; Cl, 30.02. $C_{10}H_{20}N_2Cl_2$ requires C, 50.20; H, 8.37; Cl, 29.71 per cent.)

Action of Magnesium Methyl Iodide on dl-isoNitrosothiocamphor.—An ethereal solution of isonitrosothiocamphor (15 g.) was slowly added to magnesium methyl iodide (prepared from 2.5 g. of magnesium). The blue solution changed to brown. The mixture was left overnight after which the product was decomposed by means of ice and acetic acid added just to dissolve the precipitated magnesium hydroxide. The solution was then extracted with ether and the ethereal solution dried over anhydrous sodium sulphate. After evaporation of ether, the residue gave on distillation an orange liquid, b. p. 105-106°/6 mm. It is not soluble in water, acids or alkalis, and does not form any lead salt like mercaptans; nor does it decolourise iodine. It is readily soluble in organic solvents like alcohol ether and chloroform. [Found: C, 67.84; H, 8.52; N, 7.21; S, 16.45. M. W. in benzene (cryoscopic), 195. $C_{11}H_{17}NS$ requires C, 67.69; H, 8.72; N, 7.18; S, 16.41 per cent. M. W., 195.]

Action of Methyl Iodide on isoNitrosothiocamphor in presence of Sodium Ethoxide.—Sodium (1.8 g.) was dissolved in alcohol (125 c. c.) and isonitrosothiocamphor (15 g.) added to the solution. To the mixture, methyl iodide (15 g.) was then added. The whole was heated under efficient reflux for 4 hours at 80° when the blue solution turned green. It was then diluted with ice-cold water and extracted with ether. The residue obtained from the ethereal solution gave a blue liquid, b. p. 95-100°/6 mm. The liquid is insoluble in water and in cold alkalis showing the absence of any free NOH group. [Found: C, 62.71; H, 8.12; N, 6.72; S, 15.18; M. W. cryoscopic (in benzene), 212.5. $C_{11}H_{17}ONS$ requires C, 62.56; H, 8.06; N, 6.64; S, 15.16 per cent. M. W., 211]. The blue liquid on hydrolysis with boiling dilute hydrochloric acid (1:1) gave methylmercaptan (isolated as yellow lead salt) and isonitrosocamphor, m. p. 152°.

Hydrolysis of isoNitrosothiocamphor.—A mixture of isonitrosothiocamphor (10 g.), formaldehyde (15 c. c.) and 2 drops of concentrated sulphuric acid was heated on the water-bath till it went into solution.

It was then treated with fuming hydrochloric acid (30 c. c.) and heated for 2 hours. The product was distilled in steam, when a yellow solid passed over which was subjected to fractional crystallisation from 90% alcohol. The yellow prismatic needles obtained in the first fraction melted at $197\text{--}98^\circ$ and were identical with those of camphorquinone. (Found: C, 71.65; H, 8.5. Calc. for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43 per cent). The mother liquor gave monothiocamphorquinone as greenish yellow needles, m. p. 196° . (Found C, 66.12; H, 8.02; S, 17.69. $C_{10}H_{11}OS$ requires C, 65.93; H, 7.7; S, 17.58 per cent). Monothiocamphorquinone on treatment with hydroxylamine hydrochloride and sodium hydroxide gave β -camphorquinone dioxime, m. p. 248° with evolution of sulphuretted hydrogen.

The Benzoyl Derivative.—*iso*-Nitrosothiocamphor (10 g.) was taken in benzoyl chloride (8 g.) and a 10% solution of sodium hydroxide was gradually added to the mixture. After each addition the solution became brown, the colour, however, disappeared on shaking. The separated greenish blue precipitate crystallised from dry ether as bluish green needles, m. p. $115\text{--}16^\circ$. (Found: N, 4.72; S, 10.55. $C_{17}H_{19}O_2NS$ requires N, 4.65; S, 10.63 per cent).

Isomeric form of isoNitrosothiocamphor (β -Nitroso- α -thiolbornylene).—After separation of the crystals of *l*-isomeric nitrosothiocamphor (Sen, *loc. cit.*) the turbid aqueous solution gave out mercaptanic smell. It was extracted with ether, the ethereal solution dried over anhydrous sodium sulphate, ether evaporated and the residual liquid distilled when it passed over as a blue liquid at $105\text{--}106^\circ/5$ mm. having mercaptanic smell. It is insoluble in mineral acids but dissolves in alkalis giving a yellow solution. It is also soluble in acetic acid and other organic solvents giving bluish green solutions. Owing to the extremely poor yield of the material further study has not been possible. [Found: C, 60.59; H, 7.72; N, 7.18; S, 16.23 per cent. M. W. in benzene (cryoscopic), 195. $C_{10}H_{11}ONS$ requires C, 60.91; H, 7.61; N, 7.11; S, 16.24 per cent. M. W., 197].

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