96. *Structural Changes produced in the Selenium Dehydrogenation Method. Part I. Ring Changes in* spiro-*Compounds.*

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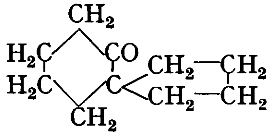
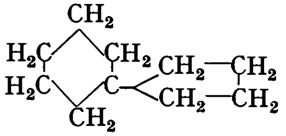
The most valuable and fruitful method of elucidating the ring structure of hydroaromatic compounds, especially the terpenes and sterols, has been the sulphur dehydrogenation method of Vesterberg (*Ber.*, 1903, **33**, 4200) and its modification using selenium (Diels, *Ber.*, 1927, **60**, 2323), which produce aromatic compounds whose structures are either known or can be ascertained by synthesis. The consequent deduction of the ring structure of the initial compound will clearly be less trustworthy if ring changes, other than extra ring formation involving a chain substituent (Diels, Gädke, and Kording, *Annalen*, 1927, **459**, 1), occur during the drastic operation which ordinarily involves heating with sulphur, or selenium, for some 36 hours at from 280° to 330°.

So far, however, no such ring changes appear to have been established, but it has now been found that some spiran compounds are transformed into aromatic structures. For instance, whilst it is already known that $\Delta^{9:10}$-octalin oxide readily gives 2-keto*cyclo*hexane*spirocyclo*pentane (I) (Hückel and co-workers, *Annalen*, 1929, **474**, 121; Clemo and Ormston, J., 1932, 1778), it has now been shown that this compound, and *cyclo*hexane*spirocyclo*pentane (II) derived from it by a Clemmensen reduction, give naphthalene on selenium dehydrogenation.

(I.)





(II.)

The compound (II) was prepared by Zelinsky and Schuikin (*Ber.*, 1929, **62**, 2180) from the hydrazone of (I) by treatment with platinum and potassium hydroxide, and they observed that, when it was treated with platinised charcoal and hydrogen at 190°, a compound $C_{10}H_{18}$ was obtained. They further state that they were unable to bring about the dehydrogenation of the latter compound at 300° in the presence of palladised asbestos or platinised charcoal.

2-*Keto*cyclo*hexane*spirocyclo*pentane*.—The ketone, obtained by the Reformatsky reaction from $\Delta^{9:10}$-octalin oxide and ethyl bromoacetate (Clemo and Ormston, *loc. cit.*), was converted into its semicarbazone, which was recrystallised five times from EtOH; m. p. 189—190°. The pure semicarbazone (3·5 g.) was shaken with $N/2$-H_2SO_4 (70 c.c.) and light petroleum (b. p. 40—60°; 30 c.c.) for 7 hr. The petroleum solution on fractionation gave 2 g. of the pure ketone, b. p. 102—103°/20 mm.

cyclo*Hexane*spirocyclo*pentane*.—The pure ketone (2 g.), amalgamated Zn (10 g.), and conc. HCl (15 c.c.) were refluxed over-night, a further 10 c.c. of acid added, and the heating continued for 7 hr. Light petroleum (b. p. 40—60°) then extracted a substance, which was dried, isolated, treated with semicarbazide hydrochloride and NaOAc in EtOH on the water-bath to eliminate any unchanged ketone, and then steam-distilled. The distillate was extracted with light petroleum, and fractionation of the extract gave *cyclo*hexane*spirocyclo*pentane (1·2 g.), b. p. 75°/20 mm. (Found: C, 87·1; H, 12·8. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%).

Dehydrogenation of the Hydrocarbon (II) *with Selenium*.—The hydrocarbon (1·2 g.) and Se (7 g.) were heated at 280—290° for 19 hr. The temp. was then raised to 320° and kept there for a further 24 hr. The reaction mixture was extracted four times with light petroleum (b. p. 40—60°), and the petroleum removed. The residue after distillation from Na at ordinary press. gave 0·24 g., part of which crystallised at once and smelt strongly of naphthalene. When the distillate was fractionated carefully under 1 mm. press., 0·1 g. of a colourless mobile oil quickly passed over, which smelt of the original hydrocarbon. The cryst. residue in the flask was distilled (0·06 g.), and crystallised from MeOH–H_2O (4 : 1), naphthalene being obtained, m. p. 80° alone or mixed with authentic naphthalene. The picrate was also prepared; m. p. 148—149°, alone or mixed with authentic naphthalene picrate.

Dehydrogenation of the Ketone (I) *with Selenium*.—The pure ketone (0·8 g.) and Se powder (5 g.) were heated together, and the reaction mixture was worked up, as described in the previous expt.; the product after distillation from Na separated into two fractions, the first of which, although it consisted largely of unchanged ketone, deposited some crystals of naphthalene. The second fraction solidified on cooling and was proved to be naphthalene as in the previous case.

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