

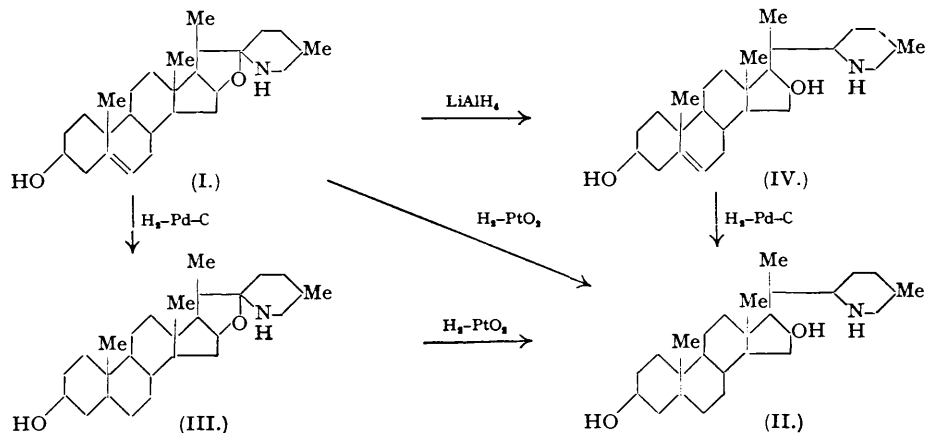
### 590. Solanum Alkaloids. Part VI. Fission of the Oxide Ring of Solasodine with Lithium Aluminium Hydride.

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The oxide ring of solasodine is reductively broken by lithium aluminium hydride with the formation of dihydrosolasodenol. Further reduction of the double bond by hydrogenation with a palladium-charcoal catalyst affords dihydrosolasodanol.

THE oxide ring of solasodine (I) (Part V, *J.*, 1950, 3013) may be opened by hydrogenolysis over an active platinum oxide catalyst, the less active palladium-charcoal catalyst being without action. The  $C_{(5)}-C_{(6)}$  double bond of solasodine is hydrogenated at the same time so that dihydrosolasodanol (II) is produced. Palladium-charcoal will, however, catalyse the hydrogenation of the double bond with the formation of solasodanol (III).

We have now found that lithium aluminium hydride brings about a ready fission of the oxide ring of solasodine without reducing the double bond. The product,  $C_{27}H_{45}O_2N$  (IV), is isomeric with solasodanol, and will be referred to as dihydrosolasodenol. The structure follows from the fact that it forms a nitrosamine and a triacetyl derivative; it is insoluble in dilute acids, and may be converted into dihydrosolasodanol by hydrogenation over a palladium-charcoal catalyst.



The absorption spectrum of dihydronitrososolasodenol shows peaks at 238  $m\mu$ . ( $\log \epsilon$  3.77) and 352  $m\mu$ . ( $\log \epsilon$  1.78), intermediate between the values of 1-nitrosopiperidine, 235  $m\mu$ . ( $\log \epsilon$  4.25) and 350  $m\mu$ . ( $\log \epsilon$  2.0) and di(cyclohexylmethyl)-*N*-nitrosamine, 240  $m\mu$ . ( $\log \epsilon$  3.9) and 355  $m\mu$ . ( $\log \epsilon$  1.95).

Solasodine hydrochloride also reacts with lithium aluminium hydride in dry ether to give dihydrosolasodenol, but in poorer yield. If solasodine had a carbinol-amine structure (cf. Part II, *J.*, 1942, 3, and Part V, *loc. cit.*), the hydrochloride should be the anhydro-salt of the quaternary ammonium hydroxide form. By analogy with the reduction of berberine sulphate

to dihydroanhydroberberine (Schmid and Karrer, *Helv. Chim. Acta*, 1949, **32**, 960), solasodine hydrochloride should have yielded solanidine. The fact that it yields dihydrosolasodenol is additional evidence for the revised formula (I) of solasodine. The opening of the oxide ring of solasodine by this method is paralleled by the ready fission of the oxide rings of sapogenins, the six-membered ring opening on catalytic hydrogenation in an acidic medium and both rings on Clemmensen reduction (Marker and Rohrmann, *J. Amer. Chem. Soc.*, 1939, **61**, 943).

#### EXPERIMENTAL.

*Dihydrosolasodenol*.—A mixture of dried solasodine (3 g.) and lithium aluminium hydride (1.5 g.) in dry ether (130 c.c.) was heated under reflux for 4½ hours with exclusion of moisture and then poured into water. The resultant precipitate consisted of finely divided alumina and organic matter. After removal of the ether, the mixture was shaken with filter-paper pulp and filtered. The dried filter-cake was shredded and extracted with alcohol in a Soxhlet apparatus. On cooling of the concentrated extract, colourless prisms were obtained. Recrystallisation of this material and that obtained by further concentration afforded *dihydrosolasodenol* (2.30 g.), m. p. 260—264° (Found: C, 77.9; H, 10.8; N, 3.6.  $C_{27}H_{45}O_2N$  requires C, 78.1; H, 10.8; N, 3.4%). Reduction of solasodine hydrochloride under similar conditions afforded the same product in smaller yield.

*Triacetyldihydrosolasodenol*. Dihydrosolasodenol (150 mg.) was heated under reflux with acetic anhydride (2 c.c.) and pyridine (0.5 c.c.) for 2 hours. The solution was poured into water, made alkaline by passage of ammonia, and set aside in the refrigerator. Repeated crystallisation, from 50% alcohol, of the precipitate which formed gave colourless, rectangular plates, m. p. 169.5—170.5° (Found: C, 72.9; H, 9.5; N, 2.4.  $C_{33}H_{51}O_5N$  requires C, 73.2; H, 9.5; N, 2.6%). The *triacetyl* derivative is insoluble in 10% acetic acid in which dihydrosolasodenol is freely soluble.

*N-Nitroso-derivative*. When a solution of sodium nitrite (250 mg.) in water (1 c.c.) was added dropwise to an ice-cool solution of dihydrosolasodenol (200 mg.) in glacial acetic acid (10 c.c.), a precipitate formed at each drop but dissolved on shaking. Only after the addition of further sodium nitrite (*ca.* 1 g. in 2.5 c.c.) did a permanent turbidity occur. After the addition of more water (20 c.c.), the mixture was set aside in the refrigerator. The white solid *nitroso*-compound (238 mg.) which formed crystallised from aqueous dioxan in colourless pointed prisms, m. p. 250—251° (decomp.) (Found: C, 73.1; H, 10.2.  $C_{27}H_{44}O_3N_2$  requires C, 73.0; H, 10.0%). The absorption spectrum measured in *ca.*  $N/5000$ -alcoholic solution in a Beckman spectrophotometer, Model D.U., is given in the figure.

Although *N*-nitrososolasodine does not give the Liebermann reaction both *N*-nitrososolasodanol and dihydro-*N*-nitrososolasodenol give a positive test.

*Hydrogenation of Dihydrosolasodenol*.—A solution of dihydrosolasodenol (150 mg.) in glacial acetic acid (3 c.c.) was hydrogenated at 45 lbs. pressure for 6 hours in the presence of palladium-charcoal (150 mg.). The filtered solution was concentrated, diluted with water, and made alkaline by passage of ammonia. The gelatinous precipitate thus produced, after three crystallisations from alcohol, separated in colourless, rhombic prisms, m. p. 288—291°, undepressed by a sample of dihydrosolasodanol, m. p. 290—294°, of the same crystalline form.

The analyses are by Drs. Weiler and Strauss, Oxford, and Dr. T. S. Ma, Microchemical Laboratory, University of Otago.

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Absorption spectrum of dihydro-*N*-nitrososolasodenol.

