23. *The Synthesis of 5-Nitroindene.*

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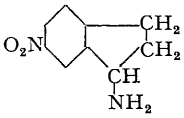
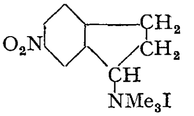
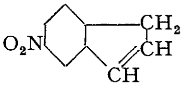
5-Nitroindene has been synthesised and its constitution established by reduction to 5-aminohydrindene.

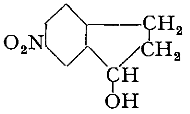
During the course of other work it became necessary to prepare 5-nitroindene (III) and if possible the simple polymeric forms, analogous for example to di-indene (Stobbe and Farbe, *Ber.*, **1924**, **57**, 1838).

Nitration of 1-hydrindamine yielded 6-nitro-1-hydrindamine (I) (Ingold and Piggott, *J.*, **1923**, 1483), which gave excellent yields of the quaternary salt (II) on methylation with methyl iodide and sodium carbonate in methyl alcoholic solution. It was hoped to prepare 5-nitroindene (III) by the action of sodium or silver hydroxide on the salt (II) but unexpected results were obtained. Although silver oxide readily converted the salt into the corresponding hydroxide, evaporation of the aqueous solution of the latter led to the elimination of trimethylamine and the precipitation of a black amorphous solid. The same substance was obtained even more conveniently by warming the iodide (II) with aqueous sodium hydroxide. Owing to the insolubility of the product, molecular weight determinations have not been possible, but the analytical results are consistent with a complex polymeric nitroindene structure. When 6-nitro-1-hydrindamine hydrochloride was warmed with sodium nitrite solution, it was converted into 6-*nitro*-1-*hydrindenol* (IV) from which a crystalline *acetate* and β-*naphthylurethane* were obtained. 6-Nitro-1-hydrindenol (IV) was converted into monomeric 5-*nitroindene* (III) by warming with 2N-hydrochloric acid. This nitro-compound (III) was volatile in steam and its constitution was established by reduction to 5-aminohydrindene and by conversion into 5-dimethylaminohydrindene methiodide.


(I.)


(II.)


(III.)


(IV.)

This monomeric 5-nitroindene did not polymerise readily and simple polymers have not been obtained by the use of hydrochloric or syrupy phosphoric acids under conditions which result in the conversion of indene into di-indene. With concentrated sulphuric acid, however, it is converted into the black insoluble polymeric form previously mentioned.

Experimental.

6-*Nitro*-1-*hydrindenol* (IV).—A solution of 6-nitro-1-hydrindamine hydrochloride (2 g.) in water (20 c.c.) was treated with sodium nitrite (0·7 g. ≡ 1 mol.) in water (5 c.c.) and after heating the solution at 100° for ½ hour it was cooled, extracted with ether, the extract dried, and the solvent removed. Distillation of the residue at 0·8 mm. gave a yellow oil (1·05 g.) which solidified; the *compound* crystallised from aqueous methyl alcohol in stout prisms, m. p. 75—77° (Found : C, 59·6; H, 5·7. $C_9H_9O_3N$ requires C, 60·0; H, 5·6%). The *acetyl* derivative, prepared in the usual way, was obtained as prisms, m. p. 52—54°, from aqueous methyl alcohol (Found : C, 60·0; H, 5·3. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%). The β-*naphthylurethane*, prepared by heating together equal weights of carbinol and β-naphthyl *iso*cyanate at 100° for two hours, was isolated as rosettes of slender rectangular prisms, m. p. 158—159°, by crystallisation from acetone–benzene (Found : C, 69·3; H, 5·0. $C_{20}H_{16}O_4N_2$ requires C, 69·0; H, 4·6%).

5-*Nitroindene* (III).—This was prepared by two methods. (*a*) 6-Nitro-1-hydrindenol (0·5 g.) and 2N-hydrochloric acid (5 c.c.) were refluxed for 20 minutes, cooled, extracted with chloroform, the extract dried, and the solvent removed. The residue crystallised from a small amount of methyl alcohol in rosettes of needles, m. p. 82—83° (0·23 g.) (Found : C, 66·8, 67·3; H, 4·9; C, 4·5. $C_9H_7O_2N$ requires 67·1; H, 4·4%). Dehydration by means of powdered potassium hydrogen sulphate at 140° gave crystalline solids of varying m. ps.—possibly mixtures of the stereoisomers of 6-nitro-1-indanyl ether (see below).

(*b*) A solution of 6-nitro-1-hydrindamine hydrochloride (2 g.) in water (20 c.c.) was heated at 100° for ¾ hour with a solution of sodium nitrite (0·7 g.) in water (5 c.c.), then concentrated hydrochloric acid (25 c.c.) added and the whole refluxed for 1½ hours. Steam distillation, followed by extraction of the distillate with chloroform and removal of the solvent, left a residue (1·27 g.) which crystallised from methyl alcohol in needles, m. p. 81—82° undepressed by admixture with the *product* from method (*a*). The non-steam-volatile residue was a sandy coloured powder, which after a preliminary crystallisation from methyl alcohol–chloroform (charcoal) was separated by fractional crystallisation into rhombic prisms, m. p. 240° (Found : C, 63·7 ; H, 5·1. $C_{18}H_{16}O_5N_2$ requires C, 63·5 ; H, 4·7%), from chloroform, and slender rectangular prisms, m. p. 176—178° (Found : C, 63·6 ; H, 4·8%), from 50% methyl alcohol. A mixture of these two *substances*—probably diastereoisomeric forms of 6-nitroindanyl ether—melted at *ca.* 160°.

5-*Aminohydrindene.*—5-Nitroindene (0·2 g.) in methyl alcohol (10 c.c.) was shaken in hydrogen in the presence of palladised charcoal (15%) (0·1 g.) until no further uptake of gas was observed. Removal of the solvent from the filtered solution gave a brownish coloured oil, which was characterised by the formation of two derivatives :

(*a*) Treatment with excess acetic anhydride and sodium acetate at 100° for ½ hour gave a white solid after removal of excess of acetic anhydride and addition of water. Crystallisation from methyl alcohol gave 5-acetamidohydrindene as prisms, m. p. 102—104° (Lindner and Bruhin, *Ber.*, 1927, **60**, 435, give m. p. 106°).

(*b*) After being refluxed overnight in methyl alcoholic solution with excess of methyl iodide and sodium carbonate, the hot solution was filtered and concentrated to half its bulk; addition of ether gave 5-dimethylaminohydrindene methiodide, m. p. 192° (decomp.), raised to 195—196°(decomp.) by recrystallisation from methyl alcohol–ether (von Braun, Arkuszewski, and Köhler, *Ber.*, 1918, **51**, 292, give m. p. 190°) (Found : equiv., 313. Calc. for $C_{12}H_{18}NI$: equiv., 303).

5-*Nitroindene Polymer*—6-Nitro-1-indanyltrimethylammonium iodide (3 g.) was heated at 100° with a solution of potassium hydroxide (0·48 g. ≡ 1 mol.) in water (20 c.c.) until a black precipitate had formed. Steam distillation removed the trimethylamine formed and the black solid (1·1 g.) was collected at the pump, washed with dilute hydrochloric acid and water, and dried at 100°. It was insoluble in all the usual organic solvents [Found : C, 66·7 ; H, 4·6 ; N, 8·52, 8·54. $(C_9H_7O_2N)_x$ requires C, 67·1 ; H, 4·4 ; N, 8·7%]. Refluxing 5-nitroindene with either syrupy phosphoric or concentrated sulphuric acid gave an insoluble brownish amorphous material indistinguishable from the *product* described above.

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