

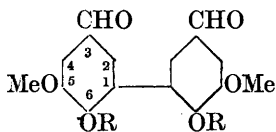
53. Nitro-derivatives of Dehydrodivanillin.

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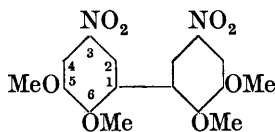
IN connexion with other investigations, it became necessary to study the nitration of derivatives of dehydrodivanillin (I), and more especially to obtain 2 : 2'-dinitrodehydrodivanillin dimethyl ether (II). By nitrating dehydrodivanillin dimethyl ether, Elbs and Lerch (*J. pr. Chem.*, 1916, **93**, 1) obtained a compound, m. p. 242°, which was not analysed. They regarded this as having the constitution (II) by analogy with their conversion of diacetyldehydrodivanillin into a dinitro-derivative, which was believed to be the 2 : 2'-dinitrodiacetyldehydrodivanillin (III).

On reinvestigating the nitration of dehydrodivanillin dimethyl ether with mixed nitric and sulphuric acids, we find that the compound, m. p. 242°, contains no aldehydo-groups, and is in reality 2 : 3 : 2' : 3' - tetranitro - 5 : 6 : 5' : 6' - tetramethoxydiphenyl (IV). Elimination of aldehydo-groups is the first result of the reaction, as was shown by the conversion of dehydrodivanillin dimethyl ether into 3 : 3'-dinitro-5 : 6 : 5' : 6'-tetramethoxydiphenyl (V) by means of cold concentrated nitric acid. The positions assigned to the nitro-groups in (IV) are selected partly on account of the 5-substitution of 4-substituted catechol ethers, and partly on account of the pronounced violet fluorescence exhibited by benzene solutions of 5 : 6 : 5' : 6' - tetramethoxydiphenyl - 2 : 3 : 2' : 3' - bisphenanthraphenazine, which is obtained by reduction of the tetranitro-compound (IV) and condensation of the resulting tetra-amino-derivative with phenanthraquinone. This phenazine is therefore to be regarded as a 2 : 3-catechol ether, rather than a 1 : 2-derivative (compare Jones and Robinson, *J.*, 1917, **111**, 910). Confirmation is thus obtained that dehydrodivanillin has the structure (I) assigned to it by Elbs and Lerch on other evidence, which is now untenable (see below).

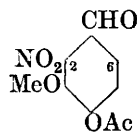
By nitrating diacetyldehydrodivanillin with mixed sulphuric and fuming nitric acids, we have obtained an aldehydic dinitro-compound, thus confirming the work of Elbs and Lerch, but the use of fuming nitric acid alone gave an increased yield of a purer product. Elbs and Lerch regarded this product as the 2 : 2'-dinitro-derivative, and based their allocation of the diphenyl linkage on this assumption. It seems rational to assume, however, that it is 4 : 4'-dinitrodiacetyldehydrodivanillin (VI), by analogy with the nitration of acetvanillin, in which 2-nitroacetvanillin (X) is formed, and not the 6-nitro-derivative (Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3405). Confirmation of this view was obtained in the following way. Alkaline hydrolysis of (VI) yielded 4 : 4'-dinitrodehydrodivanillin, which was converted into 4 : 4'-dinitrodehydrodivanillin dimethyl ether (VII) by methylation. When this substance was nitrated with mixed sulphuric and nitric acids at 50°, it yielded 2 : 3 : 4 : 3' : 4'-pentanitro-5 : 6 : 5' : 6'-tetramethoxydiphenyl (VIII), but at 0° the product was 3 : 4 : 3' : 4'-tetranitro-5 : 6 : 5' : 6'-tetramethoxydiphenyl (IX), which was different from the isomeric substance (IV).



(I.) R = H.

(II.) R = Me; NO₂ in 2 : 2'.(III.) R = Ac; NO₂ in 2 : 2'.(VI.) R = Ac; NO₂ in 4 : 4'.(VII.) R = Me; NO₂ in 4 : 4'.(IV.) NO₂ in 2 : 2'.

(V.) as written.

(VIII.) NO₂ in 2 : 4 : 4'.(IX.) NO₂ in 4 : 4'.

(X.)

EXPERIMENTAL.

Dehydrodivanillin Monomethyl Ether.—Dehydrodivanillin, obtained by the oxidation of vanillin with potassium persulphate as described by Elbs and Lerch, is sparingly soluble in the usual organic solvents, but crystallises easily from anisole in long needles, m. p. 312° [Found : C, 63.8; H, 4.9; OMe, 20.6. Calc. for C₁₄H₈O₄(OMe)₂ : C, 63.6; H, 4.6; 2OMe, 20.5%]. Elbs and Lerch give m. p. 305°.

Methylation with methyl sulphate and alkali yielded the dimethyl ether almost quantitatively, but on some occasions the alkaline filtrate contained the monomethyl ether. This filtrate was treated with charcoal, acidified, and the solid dissolved in hot alcohol, in which traces of unchanged dehydrodivanillin remained undissolved. *Dehydrodivanillin monomethyl ether* separated from the cold alcoholic solution, and, after further purification by crystallisation or conversion into the bisulphite compound and regeneration, formed colourless needles, m. p. 196° (Found : C, 64.6; H, 5.2. C₁₇H₁₆O₆

requires C, 64.6; H, 5.1%). It dissolved in sodium hydroxide and carbonate solutions and in concentrated ammonia, and was precipitated unchanged by acids. With alcoholic ferric chloride a brownish-green colour was developed. The constitution was confirmed by methylation to the dimethyl ether.

Nitration of Dehydrodivanillin Dimethyl Ether.—(A) *In concentrated nitric acid.* Dehydrodivanillin dimethyl ether (4 g.) was dissolved in cold nitric acid (d 1.42; 50 c.c.), considerable effervescence occurring. The mixture was poured into water, and the product collected and triturated with warm sodium hydrogen sulphite solution to remove traces of aldehydic material. The greater part of the product was insoluble, and after being washed with water, was crystallised from acetone (charcoal). 3 : 3'-Dinitro-5 : 6 : 5' : 6'-tetramethoxydiphenyl formed colourless needles, m. p. 215°, which were sparingly soluble in alcohol, acetone, benzene, and ether, but dissolved more readily in chloroform, acetic acid, and ethyl acetate (Found: C, 52.7; H, 4.3. $C_{16}H_{16}O_8N_2$ requires C, 52.7; H, 4.4%). It did not react with semicarbazide. It was not possible to isolate any homogeneous aldehydic substance from the bisulphite solution (above).

(B) *In mixed fuming nitric and concentrated sulphuric acids.* An unsuccessful attempt was made to follow the details given by Elbs and Lerch in which nitration was effected at -10° . The product was tarry, and yielded no recognisable substances. The following procedure, however, was satisfactory.

Dehydrodivanillin dimethyl ether (5 g.) was added gradually to a mechanically stirred mixture of nitric acid (d 1.5; 30 g.) and concentrated sulphuric acid (30 g.) maintained at -18° . The thick red liquid was poured into ice-water, and the precipitate collected, washed, dried, and crystallised twice from glacial acetic acid. 2 : 3 : 2' : 3' - Tetranitro - 5 : 6 : 5' : 6' - tetramethoxydiphenyl formed coarse yellow prisms (2 g.), m. p. 242°, which were sparingly soluble in ethyl alcohol (Found: N, 12.5. $C_{16}H_{14}O_{12}N_4$ requires N, 12.3%).

5 : 6 : 5' : 6' - Tetramethoxydiphenyl - 2 : 3 : 2' : 3' - bisphenanthra-phenazine.—The preceding tetranitro-compound was reduced in alcoholic-aqueous hydrochloric acid by means of zinc dust, the alcohol evaporated, and an excess of sodium acetate added. When this solution was mixed with a concentrated solution of phenanthraquinone in hot aqueous sodium hydrogen sulphite and the mixture was heated in the water-bath for a few minutes, a dull yellow, flocculent precipitate of the phenazine separated. It crystallised from acetone (charcoal) in yellow bipyramids which remained unmelted on being heated to 300° (Found: N, 8.1. $C_{44}H_{30}O_4N_4$

requires N, 8.3%). This substance dissolved readily in benzene, and the almost colourless solution exhibited a strong violet fluorescence.

4 : 4'-*Dinitrodiacetyldehydrodivanillin*.—Diacetyldehydrodivanillin (Elbs and Lerch, *loc. cit.*; 5 g.) was added gradually to nitric acid (*d* 1.5; 40 c.c.) stirred mechanically and maintained at -18° . The clear red liquid was poured into ice-water, and the light yellow, voluminous precipitate collected, dried, and crystallised from alcohol. 4 : 4'-*Dinitrodiacetyldehydrodivanillin* (2 g.) formed colourless needles, m. p. $85-90^{\circ}$. Elbs and Lerch also record 90° as the m. p., and the lowness of this figure, unexpected in the case of a substance of this composition, is now shown to be due to the presence of 2.5 mols. of alcohol of crystallisation which the compound lost at 100° without melting, the m. p. then rising to $168-169^{\circ}$. When recrystallised from benzene, 4 : 4'-dinitrodiacetyldehydrodivanillin had m. p. $168-169^{\circ}$ (Found: N, 5.8. $C_{20}H_{16}O_{12}N_2$ requires N, 5.9%).

4 : 4'-*Dinitrodehydrodivanillin* was obtained by dissolving the diacetyl derivative in hot 2*N*-sodium hydroxide, acidifying the hot solution with hydrochloric acid, and heating the mixture on the water-bath to coagulate the precipitate. This substance was readily soluble in methyl and ethyl alcohols, acetone, ethyl acetate, and hot acetic acid, but very sparingly soluble in benzene, toluene, carbon tetrachloride, and water. It crystallised from benzene-acetic acid in spherical clumps of microscopic yellow needles, m. p. 230° (decomp.) (Found: N, 7.4. $C_{16}H_{12}O_{10}N_2$ requires N, 7.1%).

4 : 4'-*Dinitrodehydrodivanillin dimethyl ether* was prepared by the gradual addition of methyl sulphate to a vigorously stirred, alkaline solution of 4 : 4'-dinitrodehydrodivanillin at 100° . The solution became pale yellow, and when cold, the product was collected, dried, and crystallised from benzene, from which it separated in fine colourless needles, m. p. $176-177^{\circ}$ (Found: N, 6.6. $C_{18}H_{16}O_{10}N_2$ requires N, 6.7%).

2 : 3 : 4 : 3' : 4' - *Pentanitro - 5 : 6 : 5' : 6' - tetramethoxydiphenyl*.—4 : 4'-Dinitrodehydrodivanillin dimethyl ether (106 mg.) was added to 2 c.c. of a mixture consisting of nitric acid (*d* 1.48; 5 c.c.) and concentrated sulphuric acid (2 c.c.). Vigorous effervescence occurred, accompanied by a rise in temperature. When the solution began to cool, the mixture was warmed to 50° for 1 minute, cooled, and mixed with water. The solid was collected, washed with water, and dilute sodium carbonate solution (no red coloration), and heated with concentrated aqueous sodium hydrogen sulphite. The solid became oily, then hardened, and was collected and crystallised from alcohol. *Pentanitrotetramethoxydiphenyl* formed stout yellow prisms, m. p. 175° [Found: C, 37.3, 37.3; H, 2.6, 2.6; N, 14.0; OMe, 24.0.

$C_{12}H_{10}N_5(OMe)_4$ requires C, 38.5; H, 2.6; N, 14.0; 4OMe, 24.8%]. A mixture with 4:4'-dinitrodehydrodivanillin dimethyl ether melted at 145—150°.

3 : 4 : 3' : 4' - *Tetranitro-5 : 6 : 5' : 6' - tetramethoxydiphenyl*.—4 : 4' - Dinitrodehydrodivanillin dimethyl ether (25 mg.) was dissolved in an ice-cold mixture of nitric acid (d 1.48; 0.5 c.c.) and concentrated sulphuric acid (0.2 c.c.). When the evolution of gas had ceased, the mixture was poured into water, and the solid was collected, washed with water, sodium carbonate solution (no red coloration), and hot sodium hydrogen sulphite solution, and crystallised from alcohol. 3 : 4 : 3' : 4' - *Tetranitro-5 : 6 : 5' : 6' - tetramethoxydiphenyl* formed cream-coloured columns, m. p. 197° (Found : N, 12.8. $C_{16}H_{14}O_{12}N_4$ requires N, 12.3%). The amount of this substance at our disposal was unfortunately insufficient for more than this nitrogen estimation, and we are not in a position to prepare a further supply. The constitution of this substance cannot therefore be established with certainty, but a consideration of its properties and those of the pentanitro-compound (above), taken in conjunction with their modes of formation, leaves little doubt that the constitution assigned is correct.

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