164. *The Nitration of* O-*Benzylvanillin.*

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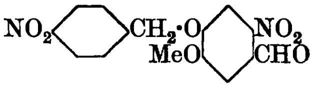
6-*Nitrovanillin* (II), required for synthetic work, has now been prepared. Into *O*-benzylvanillin, under all the conditions of nitration tried, two nitro-groups were introduced, the main product being O-p-*nitrobenzyl*-6-*nitrovanillin* (I), accompanied by the isomeric *o*-nitrobenzyl ether in smaller relative amount. These substances were also obtained by the nitration of *vanillin* p-*nitrobenzyl* and o-*nitrobenzyl ethers*, respectively.

The position of the nitro-group in the catechol nucleus of (I) was determined by oxidation of the aldehyde to a carboxylic acid which, on nitration, furnished the *p*-nitrobenzyl ether of 4 : 5-dinitroguaiacol, from which, by hydrolysis and methylation, the characteristic 4 : 5-dinitroveratrole was derived. 6-Nitrovanillin was obtained by the hydrolysis of (I) and yielded the known 6-nitroveratraldehyde on methylation.

(I.)



(II.)

The products of the nitration of benzylvanillin are all aldehydic in character and replacement of the formyl group, which occurs in the nitration of piperonal and veratraldehyde, does not appear to take place. We conclude from this that the nitrating agent first attacks the benzyl group, the directive power of which is thus greatly weakened in comparison with methoxyl (compare Oxford and Robinson, J., 1926, 383).

EXPERIMENTAL.

O-p-*Nitrobenzylvanillin*.—A mixture of vanillin (4·6 g.), *p*-nitrobenzyl chloride (5·1 g.), potassium carbonate (1·5 g.), and acetone (60 c.c.) was refluxed for 7—8 hours and then added to water. The product (6·3 g.) crystallised from alcohol in colourless needles, m. p. 124° (Found : C, 62·5; H, 4·5; N, 5·0. $C_{15}H_{13}O_5N$ requires C, 62·7; H, 4·6; N, 4·9%). It is readily soluble in cold acetone and ethyl acetate and in hot ethyl alcohol.

The o-*nitrobenzyl* ether, prepared in a similar manner (yield, almost theoretical), crystallised from alcohol in colourless needles, m. p. 128—130° (Found : C, 62·4; H, 4·5; N, 5·0%). Hydrolysis with hot concentrated hydrochloric acid furnished vanillin and *o*-nitrobenzyl chloride.

O-p-*Nitrobenzyl-6-nitrovanillin* (I).—Powdered *O*-benzylvanillin (25 g.) was gradually added to nitric acid (120 c.c.; *d* 1·46), mechanically stirred at 0°. After 1 hour the whole was added to ice, and the solid product crystallised 10 times from ethyl acetate (mother-liquor, M), giving pale yellow, slender needles (21 g.), m. p. 212—214° (Found: C, 54·3; H, 3·7; N, 8·5. $C_{15}H_{12}O_7N_2$ requires C, 54·2; H, 3·6; N, 8·4%). This substance is very sparingly soluble in alcohol, chloroform and ether and somewhat readily soluble in acetone and pyridine and in hot ethyl acetate, acetic acid, and benzene. Like many other *o*-nitrobenzaldehydes, it becomes deep yellow when exposed to light. It does not yield smoothly a substituted indigotin by the Baeyer–Drewsen method (compare Pisovschi, *Ber.*, 1910, **43**, 2139, for the similar behaviour of 6-nitroveratraldehyde).

The *phenylhydrazone* crystallised from acetic acid or aqueous alcohol in brick-red needles, m. p. 208° (Found: N, 13·4. $C_{21}H_{18}O_6N_4$ requires N, 13·3%), the *oxime* from alcohol in pale yellow needles, m. p. 158—160° (Found: N, 11·9. $C_{15}H_{13}O_7N_3$ requires N, 12·1%), and the *phenylimine* (obtained by heating the aldehyde with twice its weight of aniline on the steam-bath for 20 minutes) from alcohol in yellow prisms, m. p. 192—193° (Found: N, 10·4. $C_{21}H_{17}O_6N_3$ requires N, 10·3%), becoming deep orange on exposure to light.

O-*p*-Nitrobenzyl-6-nitrovanillin was also prepared by nitration of *O*-*p*-nitrobenzylvanillin under conditions similar to those described above; crystallised from ethyl acetate, it had m. p. 212—213° and, mixed with the specimen from *O*-benzylvanillin, 213°.

6-*Nitrovanillin* (II).—A mixture of pure *O*-*p*-nitrobenzyl-6-nitrovanillin (10 g.) and concentrated sulphuric acid (80 c.c.) was kept at 50° for 30 minutes and then at 50—60° for 2½ hours. The cooled viscous liquid was added to ice, and the brownish-red solid crystallised alternately from water and from alcohol (animal charcoal), pale yellow needles (2·2 g.), m. p. 207°, being ultimately isolated (Found: C, 48·6; H, 3·6; N, 7·2. $C_8H_7O_5N$ requires C, 48·7; H, 3·5; N, 7·1%). Exposed to light, this substance rapidly becomes deep yellow; it is moderately readily soluble in hot water and most organic solvents and in aqueous sodium carbonate to a reddish-yellow solution.

The *phenylhydrazone* crystallised from benzene in dark red needles, m. p. 198° (Found: N, 14·8. $C_{14}H_{13}O_4N_3$ requires N, 14·6%).

On methylation by means of aqueous potassium hydroxide and methyl sulphate, the nitrovanillin yielded its own weight of 6-nitroveratraldehyde, yellow needles from boiling water, m. p. 132°, alone or mixed with an authentic specimen.

O-p-*Nitrobenzyl-6-nitrovanillic Acid.*—A hot aqueous solution of potassium permanganate (120 c.c. of 10%) was gradually added to a vigorously stirred, boiling solution of *O*-*p*-nitrobenzyl-6-nitrovanillin (10 g.) in acetone (700 c.c.). After 1 hour, water (100 c.c.) was added, the acetone removed by distillation of the filtered solution, and the aqueous solution separated from the unchanged material which was deposited at this stage. The *acid*, obtained as a voluminous white precipitate on acidification, crystallised from aqueous acetone or aqueous alcohol in slender needles (9·5 g.), m. p. 208° (Found: C, 51·5; H, 3·5; N, 8·1. $C_{15}H_{12}O_8N_2$ requires C, 51·7; H, 3·5; N, 8·1%).

O-p-*Nitrobenzyl*-4 : 5-*dinitroguaiacol*, produced by boiling the foregoing acid (3 g.) with nitric acid (20 c.c.; *d* 1·42) for 20 minutes, crystallised from toluene in pale yellow prisms (2·5 g.), m. p. 178—180° (Found: C, 47·9; H, 3·2; N, 11·9. $C_{14}H_{11}O_8N_3$ requires C, 48·1; H, 3·2; N, 12·0%), readily soluble in acetone, pyridine, and carbon disulphide and sparingly soluble in alcohol, benzene, acetic acid, and ethyl acetate.

Hydrolysis was effected by refluxing 3 g. for 2 hours with acetic acid (15 c.c.) and hydrobromic acid (15 c.c. of 50%). The phenolic product was then methylated by means of aqueous potassium hydroxide and methyl sulphate in excess and the neutral material was isolated; after crystallisation it had m. p. 130·5°, alone or mixed with authentic 4 : 5-dinitroveratrole.

O-o-*Nitrobenzyl*-6-*nitrovanillin.*—The ethyl acetate mother-liquors (M) were concentrated and a pale yellow substance was precipitated by addition of light petroleum. This material was crystallised from alcohol and thus separated from the *p*-isomeride, which is not appreciably soluble in this solvent, even when boiling. After 10 crystallisations the o-*nitrobenzyl* ether was obtained pure (7·0 g.) in pale yellow plates, m. p. 174—176° (Found: C, 53·8; H, 3·7; N, 8·5. $C_{15}H_{12}O_7N_2$ requires C, 54·2; H, 3·6; N, 8·4%).

The hydrolysis of this substance, under conditions similar to those employed for the *p*-isomeride, afforded 6-nitrovanillin.

The product of nitration of *O*-*o*-nitrobenzylvanillin by means of cold nitric acid (*d* 1·46) had m. p. 174—175° (mixed m. p. 175°), and this fact demonstrates not only the constitution of the substance but also the completeness of the separation of the isomerides by fractional crystallisation.

The *phenylhydrazone* crystallised from acetic acid or aqueous alcohol in dark red needles, m. p. 190—192° (Found: N, 13·2. $C_{21}H_{18}O_6N_4$ requires N, 13·3%), the *oxime* from alcohol in pale yellow needles, m. p. 142—144° (Found: N, 12·0. $C_{15}H_{13}O_7N_3$ requires N, 12·1%), and the *phenylimine* from alcohol in yellow needles, m. p. 138—140° (Found : N, 10·4. $C_{21}H_{17}O_6N_3$ requires N, 10·3%), becoming orange on exposure to light.

O-o-*Nitrobenzyl*-6-*nitrovanillic Acid*.—The oxidation of *o*-nitrobenzyl-6-nitrovanillin was carried out like that of the *p*-nitrobenzyl ether and gave equally satisfactory results. The product crystallised from hot water or from aqueous acetone in colourless needles, m. p. 201—202° (Found : C, 51·5; H, 3·4; N, 8·0. $C_{15}H_{12}O_8N_2$ requires C, 51·7; H, 3·5; N, 8·1%). The *acid* is more readily soluble in hot water than the *p*-isomeride, but resembles it in other respects. When it was boiled with nitric acid, and the product hydrolysed and methylated, 4 : 5-dinitroveratrole was obtained.

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