448. *Some Alkylresorcinols.*

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A number of alkylresorcinols, mainly of formula $C_9H_{12}O_2$, have been prepared in the course of the identification of 5-ethyl-4-methylresorcinol from citrinin (*loc. cit.*). The phenols have been characterised by the formation of di-*p*-nitrobenzoates.

The isomeric alkylresorcinols $C_9H_{12}O_2$ and their derivatives described in the present communication were synthesised in the course of studies on the identification of 5-ethyl-4-methylresorcinol obtained originally by the degradation of citrinin (*J.*, 1949, 859). Except in the case of 5-ethyl-2-methylresorcinol, the phenols described have been characterised by the formation of di-*p*-nitrobenzoates as well as by the formation of bisphenylazo-derivatives in some instances. In connection with the three isomeric *iso*propylresorcinols it is of interest that Meyer and Bernhauer (*Monatsh.*, 1929, **53**, 721) obtained an *iso*propylresorcinol, m. p. 107°, believed to be probably 4-*iso*propylresorcinol by the condensation of resorcinol and *iso*propyl alcohol with sulphuric acid. Repetition of this experiment gave a compound, m. p. 107—108°, which was not identical with either 2-*n*-propyl-, 4-*iso*propyl-, or 5-*iso*propyl-resorcinol.

EXPERIMENTAL.

4-*Ethyl*-2-*methylresorcinol*.—3-Ethyl-6-methoxy-*o*-cresol (Me = 1) (3·6 g.) was prepared from 2-hydroxy-4-methoxy-3-methylacetophenone (Rangaswami and Seshadri, *Proc. Indian Acad. Sci.*, 1938, **8**, *A*, 214) by the method of Robinson and Shah (*J.*, 1934, 1491) and on demethylation with boiling hydriodic acid (25 ml.; *d* 1·7) and acetic acid (from 15 ml. of acetic anhydride) for ½ hour gave rise to 4-ethyl-2-methylresorcinol which was purified by distillation in a vacuum (b. p. 108°/0·4 mm.) and then by crystallisation from benzene–light petroleum (b. p. 60—80°), forming needles, m. p. 92—93° (Found : C, 71·0; H, 8·2. Calc. for $C_9H_{12}O_2$: C, 71·0; H, 8·0%) (cf. Robinson and Shah, *loc. cit.*, who give m. p. 88—90°). This compound was also prepared by Clemmensen reduction of 2 : 4-dihydroxy-3-methylacetophenone. The *di*-p-*nitrobenzoate* separated from alcohol in pale yellow needles, m. p. 146° (Found : N, 6·6. $C_{23}H_{18}O_8N_2$ requires N, 6·2%).

5-*Ethyl*-2-*methylresorcinol*.—A well stirred mixture of 3 : 5-dimethoxy-4-methylacetophenone (0·8 g.) (*J.*, 1950, 2971), benzene (25 ml.), concentrated hydrochloric acid (25 ml.), and amalgamated zinc (7 g.) was heated on the steam-bath for 2½ hours. Dimethyl ether of 5-ethyl-2-methylresorcinol was obtained as a pale orange oil (0·6 g.) which on demethylation with boiling hydriodic acid (10 ml.; *d* 1·7) and acetic acid (from 6 ml. of anhydride) gave 5-*ethyl*-2-*methylresorcinol* which was obtained in prismatic needles, m. p. 121—122°, after repeated sublimation at 120—130°/0·05 mm., having a transient blue ferric reaction in aqueous alcohol (Found : C, 71·3; H, 8·2. $C_9H_{12}O_2$ requires C, 71·0; H, 8·0%).

2-*Ethyl*-4-*methylresorcinol*.—3-Ethyl-2 : 4-dihydroxybenzaldehyde (cf. Robinson and Shah, *loc. cit.*) had m. p. 122° and on reduction gave 2-ethyl-4-methylresorcinol, m. p. 99—100°, which gave a *di*-p-*nitrobenzoate*, prisms, m. p. 158—159° (from alcohol) (Found : N, 6·3%).

2-*Ethyl*-5-*methylresorcinol*.—This phenol (Desai and Vakil, *Proc. Indian Acad. Sci.*, 1940, **12**, *A*, 39, who give m. p. 135°) formed rosettes of needles, m. p. 132°, from benzene and had a blue ferric reaction in water. The *di*-p-*nitrobenzoate* separated from alcohol–ethyl acetate in prisms, m. p. 163—164° (Found : N, 6·3%), and the *bisphenylazo*-derivative in orange leaflets, m. p. 192°, from light petroleum (Found : N, 15·4. $C_{21}H_{20}O_2N_4$ requires N, 15·6%).

4-*Ethyl*-5-*methylresorcinol*.—Prepared by the method of Robinson and Shah (*loc. cit.*) who give m. p. 75—80°, 4-ethyl-5-methylresorcinol formed needles, m. p. 82—83°, from benzene and gave a *di*-p-*nitrobenzoate*, separating from alcohol in needles, m. p. 171—171·5° (Found : C, 61·5; H, 4·2; N, 5·9. $C_{23}H_{18}O_8N_2$ requires C, 61·3; H, 4·0; N, 6·2%). On being warmed with diazoaminobenzene (1·2 g.) in alcohol (15 ml.) on the steam-bath for 1 hour this phenol (0·2 g.) gave rise to the *bisphenylazo*-derivative which formed red needles, m. p. 184°, from alcohol and orange plates, m. p. 193°, from light petroleum (Found: C, 69·7; H, 5·8; N, 15·7. $C_{21}H_{20}O_2N_4$ requires C, 70·0; H, 5·6; N, 15·6%).

4-*Ethyl*-6-*methylresorcinol*.—This compound was prepared by the reduction of 2 : 4-dihydroxy-5-ethylbenzaldehyde, m. p. 134°, and obtained as a colourless oil, b. p. 110°/0·05 mm., which crystallised in needles, m. p. 56° (Found : C, 70·9; H, 8·2%) (cf. Robinson and Shah, *loc. cit.*, who give m. p. 60—63°). Purification of this phenol from benzene–light petroleum gave material containing solvent of crystallisation. The *di*-p-*nitrobenzoate* separated from dilute alcohol or acetic acid in pale yellow, slender needles, m. p. 148—149° (Found : C, 61·2; H, 4·0; N, 6·1%).

The *di*-p-*nitrobenzoate* of 2-*n*-propylresorcinol (Limaye and Shenoliker, *Rasayanam*, 1936, **1**, 93) separated from alcohol in pale yellow prisms, m. p. 163° (Found : N, 6·1. $C_{23}H_{18}O_8N_2$ requires N, 6·2%).

Contrary to Sonn (*Ber.*, 1921, **54**, 774), who stated that 4-*n*-propylresorcinol had m. p. 107—108°, whilst the solvated compound had m. p. 71°, we found that, prepared by the method of Johnson and Lane (*J. Amer. Chem. Soc.*, 1921, **43**, 357), who give m. p. 78°, this phenol had m. p. 78—79°. The *di*-p-*nitrobenzoate* formed rosettes of pale yellow needles, m. p. 133°, from alcohol (Found : N, 6·4%). The *bisphenylazo*-derivative separated from light petroleum in crimson needles, m. p. 168° (Found : N, 15·7. $C_{21}H_{20}O_2N_4$ requires N, 15·6%).

5-*Ethyl*-4-n-*propylresorcinol*.—The interaction of 5-ethylresorcinol (2 g.), propionitrile (1·5 g.), and zinc chloride (2·5 g.) in ether (100 ml.), saturated with hydrogen chloride, during 2 days gave an oil which was washed with ether by decantation. A solution of this product in water (75 ml.) was almost neutralised with sodium hydrogen carbonate and then heated on the steam-bath for 45 minutes, giving 5-*ethyl*-2 : 4-*dihydroxy*-n-*propiophenone* which formed colourless prisms (0·6 g.), m. p. 142°, from benzene and had a red-brown ferric reaction in alcohol (Found : C, 68·2; H, 7·5. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%). Reduction of this ketone (0·5 g.), by Clemmensen's method gave 5-*ethyl*-4-n-*propylresorcinol*, separating from benzene–light petroleum in glistening plates, m. p. 78° (Found : C, 73·5; H, 9·1. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%). The *di*-p-*nitrobenzoate* crystallised from alcohol in long colourless needles, m. p. 148° (Found : C, 62·6; H, 4·8; N, 6·1. $C_{25}H_{22}O_8N_2$ requires C, 62·8; H, 4·7; N, 5·9%), and the *bisphenylazo*-derivative in scarlet needles, m. p. 181° (Found : N, 14·5. $C_{23}H_{24}O_2N_4$ requires N, 14·4%).

2-iso*Propylresorcinol*.—A solution of 2 : 6-dimethoxyacetophenone (Sugusawa, *J.*, 1934, 1483) (6·2 g.) in benzene (90 ml.) was added to well-stirred ethereal methylmagnesium iodide (from 5 g. of magnesium, 35 g. of methyl iodide, and 100 ml. of ether), the ether was evaporated, the benzene liquor was heated under reflux on the steam-bath for 4 hours, and then after the evaporation of the benzene the viscous residue was kept at 100° for 2 hours. Next day the product was covered with ether (100 ml.) and decomposed with saturated aqueous ammonium chloride (100 ml.). On isolation with ether the resulting 2-(2 : 6-*dimethoxyphenyl*)*propene* was obtained as a colourless oil (5·9 g.), b. p. 106—110°/0·15 mm. (Found : C, 74·3; H, 8·1. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%). Hydrogenation of this propene (5 g.), dissolved in methanol (150 ml.), with the palladium–charcoal catalyst gave rise to 2-(2 : 6-*dimethoxyphenyl*)*propane* as a colourless oil (4·7 g.), b. p. 71—73°/0·05 mm. (Found : C, 73·2; H, 9·1. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%).

Demethylation of the foregoing propane derivative (1·6 g.) with boiling hydriodic acid (25 ml., *d* 1·7) and acetic acid (from 15 ml. of anhydride) during ½ hour furnished 2-iso*propylresorcinol*, b. p. 114°/0·05 mm., which crystallised from benzene–light petroleum in rosettes of colourless needles, m. p. 82°, having a pale blue ferric reaction in water (Found : C, 71·2; H, 8·2. $C_9H_{12}O_2$ requires C, 71·0; H, 8·0%). The *di*-p-*nitrobenzoate* separated from acetic acid in pale yellow small needles, m. p. 184—185° (Found : N, 6·2%).

4-iso*Propylresorcinol*.—Prepared from 2 : 4-dimethoxyacetophenone (4 g.) by the method employed for 2-(2 : 6-dimethoxyphenyl)propene, 2-(2 : 4-*dimethoxyphenyl*)*propene* (3 g.) was obtained as a colourless pungent oil, b. p. 170°/10 mm. (Found : C, 73·6; H, 8·2%), which on hydrogenation, yielded 2-(2 : 4-dimethoxyphenyl)propane. Demethylation of the foregoing propane (2 g.) in the usual manner furnished 4-iso*propylresorcinol* which was purified by distillation in a vacuum and then by crystallisation from benzene, forming large colourless prisms (1·1 g.), b. p. 114°/0·2 mm., m. p. 98°, moderately soluble in benzene or water and giving a blue ferric reaction in water (Found : C, 70·9; H, 8·1%). The *di*-p-*nitrobenzoate* separated from acetic acid in needles, m. p. 124° (Found : C, 61·3; H, 4·0; N, 6·2%), and the *bisphenylazo*-derivative from alcohol in two interconvertible forms : (*a*) flocculent orange needles, m. p. 186° with sintering at 166°, and (*b*) purple-red needles, m. p. 186° after sintering at 183° (Found : C, 70·0; H, 5·7; N, 15·6. $C_{21}H_{20}O_2N_4$ requires C, 70·0; H, 5·6; N, 15·6%).

5-iso*Propylresorcinol*.—The quantitative formation of methyl 3 : 5-dimethoxybenzoate from the parent acid with diazomethane was found to be superior to Seka and Fuchs's lengthy esterification process (*Monatsh.*, 1931, **57**, 65). This ester (10·1 g.) was heated under reflux with ethereal methylmagnesium iodide (from 14·7 g. of magnesium, 43 ml. of methyl iodide, and 360 ml. of ether) for 6 hours and the mixture treated with ice and aqueous ammonium chloride. The resulting 2-(3 : 5-*dimethoxyphenyl*)-*propene* was purified by distillation and obtained as a colourless oil (5·9 g.), b. p. 134°/15 mm. (Found : C, 74·4; H, 8·1. $C_{11}H_{14}O_2$ requires C, 74·0; H, 7·9%). On hydrogenation with a palladium–charcoal catalyst this compound gave a quantitative yield of 2-(3 : 5-*dimethoxyphenyl*)*propane*, a colourless oil, b. p. 125°/1·4 mm. (Found : C, 73·6; H, 9·2. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%).

Demethylation of the foregoing propane derivative (4 g.) by boiling concentrated hydriodic acid–acetic acid during ½ hour furnished 5-iso*propylresorcinol* which was purified by distillation and then by crystallisation from benzene, forming colourless prisms (2·7 g.), b. p. 120°/0·15 mm., m. p. 110°, readily soluble in water and having a violet ferric reaction in alcohol (Found : C, 71·3; H, 8·1%). The *di*-p-*nitrobenzoate* separated from acetic acid in pale cream-coloured prisms, m. p. 183° (Found : C, 61·2; H, 4·2; N, 6·1%), and the *bisphenylazo*-derivative from alcohol in orange needles, m. p. 190° (Found : C, 70·0; H, 5·2; N, 15·3%).

Colour Reactions of Alkylresorcinols.—In examining qualitative methods for the differentiation of substituted resorcinols it has been observed that with aqueous bleaching powder resorcinol, orcinol, 5-ethyl-, 5-*n*-propyl-, and 5-*iso*propyl-resorcinol give cherry-red colours fading to reddish-brown, whereas γ-alkylresorcinols, *e.g.*, 2-methyl-, 2-ethyl-, 2-*n*-propyl-, 2-*iso*propyl-, 2-ethyl-4-methyl-, 2-ethyl-5-methyl-, and 4-ethyl-2-methyl-resorcinol, give comparatively stable red or bluish-red colours. On the other hand, yellow or orange-yellow colours are given by β-substituted resorcinols of the following types : 4-methyl-, 4-*n*-propyl-, 5-ethyl-4-methyl-, 6-ethyl-4-methyl-, and 4-ethyl-5-methyl-resorcinol.

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