NOTES.

Nuclear Methylation of α-Naphthol. A Correction.

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We recently reported (J., 1942, 682) that the action of methanolic sodium methoxide on 4-piperidinomethyl-1-naphthol afforded 4-methyl-1-naphthol. This was the expected product and the m. p. 84—85° and other properties agreed with the description by Lesser (*Annalen*, 1914, **402**, 8).

It has now been found that a mixture with authentic 4-methyl-1-naphthol shows a large depression and the substance is 2 : 4-*dimethyl*-1-*naphthol* (15 g. from 50 g. of piperidinomethyl-1-naphthol), m. p. 84—85°, b. p. 169—170°/10 mm. (Found : C, 83·4; H, 7·0; active H, 0·53. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0; 1H, 0·59%). The *picrate* crystallises from aqueous alcohol in dark red needles, m. p. 143—144° (Found : N, 10·6. $C_{12}H_{12}O,C_6H_3O_7N_3$ requires N, 10·5%). Oxidation by means of alkaline permanganate afforded phthalic acid. Whereas 1-naphthol, 2-methyl-1-naphthol, and 4-methyl-1-naphthol couple with *p*-nitrobenzenediazonium chloride in aqueous alcoholic sodium hydroxide solution with formation of a deep blue coloration, this dimethylnaphthol gives only a dull red colour. In aqueous alkaline solution, gradually treated with acetic acid, coupling occurs near the neutral point and the precipitated azo-compound gives the blue solution in alcoholic sodium hydroxide. This experiment indicates the displacement of a methyl group. The formulation of piperidinomethyl-1-naphthol as a 4-derivative by Auwers and Dombrowski (*Annalen*, 1905, **344**, 289) was not supported by direct evidence, and by analogy Feldman and Wagner (*J. Org. Chem.*, 1942, **7**, 31) have suggested that it is 2-piperidinomethyl-1-naphthol. Experimental proof of the correctness of this view is provided by the reduction of the base to 2-methyl-1-naphthol. Hydrogenation was effected in alcoholic solution at 165°/100 atm. in presence of copper chromite. The phenolic product was sublimed under diminished pressure and crystallised from light petroleum, forming long needles, m. p. 64—65°, agreeing in this and other properties with the description of Veselý and Páx (*Coll. Trav. chim. Tchecoslovaquie*, 1930, **2**, 471). The *picrate* separated from aqueous alcohol in bright red needles, m. p. 133—134° (Found: N, 10·7. $C_{11}H_{10}O,C_6H_3O_7N_3$ requires N, 10·9%).—Dyson Perrins Laboratory, Oxford University. [*Received, March 2nd*, 1943.]

4-*Nitro*-3-*ethoxytoluene*-6-*sulphonic Acid.*

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Conditions for the preparation of 4-nitro-3-ethoxytoluene-6-sulphonic acid from 3-ethoxytoluene are described. The positions of the nitro- and the sulpho-group are established by (i) the preparation of the same substance from 4-nitro-3-ethoxytoluene and (ii) the formation of 6-nitro-3-ethoxytoluene by nitration of 3-ethoxytoluenesulphonic acid. Further products of nitration of this acid are the 2-nitro- and the 2 : 4-dinitro-sulphonic acid. The oxidation of the nitro-sulphonic acid gave only traces of the expected stilbene.

3-*Ethoxytoluene*-6-*sulphonic Acid* (*Sodium Salt*).—3-Ethoxytoluene (100 g.) was added gradually to concentrated sulphuric acid (150 c.c.) below 30°. After 12 hours the product was added to saturated brine (300 c.c.), and the resulting solid crystallised from water and dried at 105°. It gave a *sulphonyl chloride*, b. p. 176—177°/10 mm. (Found : C, 46·0; H, 4·9. $C_9H_{11}O_3ClS$ requires C, 46·0; H, 4·7%), sulphonamide, m. p. 113—114° (Huntress and Carten, *J. Amer. Chem.*

Soc., 1940, **62**, 603, give m. p. 110—111°) (Found : C, 50·4; H, 5·9. Calc. : C, 50·2; H, 6·0%), and a p-*toluidine* salt, m. p. 100—120° (Found : C, 56·8; H, 6·9. $C_9H_{12}O_4S,C_7H_7{\cdot}NH_2,H_2O$ requires C, 56·3; H, 6·7%. Specimen dried in a vacuum over potash).

Sulphonation of 4-*Nitro*-3-*ethoxytoluene.*—The nitro-ether (6 g.) was added gradually to chlorosulphonic acid (4 g.) at 20°. After standing overnight, the mixture was treated with water, and the aqueous solution decanted, treated with charcoal, and added to saturated brine. The resulting solid was dried and extracted with hot alcohol, from which sodium 4-nitro-3-ethoxytoluene-6-sulphonate separated on cooling. It gave a p-*toluidine* salt, m. p. 232—233°, from water (Found : C, 52·05; H, 5·3. $C_9H_{11}O_6NS,C_7H_9N$ requires C, 52·2; H, 5·4%), and a *sulphonyl chloride*, m. p. 110—111°, from ligroin (Found : C, 38·7; H, 3·6. $C_9H_{10}O_5NClS$ requires C, 38·6; H, 3·6%).

Nitration of 3-*Ethoxytoluene*-6-*sulphonic Acid.*—(a) *Preparation of* 4-*nitro*-3-*ethoxytoluene*-6-*sulphonic acid.* Concentrated sulphuric acid (200 g.) was slowly added to 3-ethoxytoluene (100 g.) at *ca.* 30°, and the mixture left for 12 hours at 30—35° to prevent crystallisation. A mixture of nitric acid (47 c.c., *d* 1·42) and concentrated sulphuric acid (100 c.c.) was then added at such a rate that the temperature was maintained at 15—18° by a bath of melting ice (1—1½ hours). The whole was kept at room temperature for 1½ hours, sometimes becoming almost solid, and was then added to ice (200 g.). The heat evolved sufficed to give a dark red solution, from which, on cooling, crystals of 4- and 2-nitro-3-ethoxytoluene-6-sulphonic acids separated. After filtration (filtrate I), the solid, pressed dry (pump), was dissolved in warm water (100 c.c.), from which the 4-nitro-isomer separated (70—80 g.) (filtrate II). It contained a small amount of neutral material, which was removed by recrystallisation from water or in the process of conversion into the sodium salt. It gave a *p*-toluidine salt and a sulphonyl chloride identical with the specimens prepared as described above.

(b) *Isolation of other products.* (i) 6-*Nitro*-3-*ethoxytoluene.* The solution obtained by sulphonating 10 g. of 3-ethoxytoluene with 20 g. of concentrated sulphuric acid was added with cooling to 8 c.c. of water and nitrated by addition of concentrated nitric acid (5 c.c.) at 10—15° during 30 mins. After standing for 1 hour at 15—20°, the mixture was poured into water (100 c.c.). The precipitated solid (6·5 g.) was washed with dilute caustic soda solution and with water and recrystallised from alcohol (30 c.c.); it then had m. p. 52—53°, undepressed by 6-nitro-3-ethoxytoluene.

(ii) *Sodium* 2 : 4-*dinitro*-3-*ethoxytoluene*-6-*sulphonate.* Sodium 3-ethoxytoluene-6-sulphonate (12 g.) was dissolved in concentrated sulphuric acid (20 c.c.) and nitrated with nitric acid (2·5 c.c., *d* 1·5) below 30°. After standing overnight, the mixture was poured into water (100 c.c.). The insoluble residue (about 1 g.) was filtered off, and the sodium salt (6·5 g.) precipitated by addition of sodium chloride. The p-*toluidine* salt, crystallised from water, had m. p. 225—227° (decomp.) (Found : C, 46·6; H, 4·7; N, 10·3. $C_9H_{10}O_8N_2S,C_7H_9N$ requires C, 46·5; H, 4·6; N, 10·2%). The *sulphonyl chloride* had m. p. 104° (Found : C, 33·6; H, 3·1. $C_9H_9O_7N_2ClS$ requires C, 33·3; H, 2·8%).

Nitration of the sulphonic acid (from 10 g. of 3-ethoxytoluene and 20 g. of concentrated sulphuric acid) with nitric acid (*d* 1·5) gave the same dinitro-sulphonic acid (6 g. of sodium salt) together with 4 : 6-dinitro-3-ethoxytoluene (1·5 g. approx.) and sodium 4-nitro-3-ethoxytoluene-6-sulphonate (3 g. approx.).

Filtrate I above gave the same salt on partial neutralisation with sodium carbonate.

(iii) Sodium 2-nitro-3-ethoxytoluene-6-sulphonate was obtained from filtrate II above on almost complete neutralisation with sodium carbonate; it crystallised from water (in bulk) in characteristic shining plates (25 g.). The *p*-toluidine salt was gelatinous; the *sulphonyl chloride* had m. p. 97° (Found : C, 38·6; H, 3·5; N, 5·1. $C_9H_{10}O_5NClS$ requires C, 38·6; H, 3·6; N, 5·0%).

Oxidation of Sodium 4-*Nitro*-3-*ethoxytoluene*-6-*sulphonate.*—(*a*) The sodium salt (10 g.) in water (200 c.c.) was heated at 50—55° for 5 hours with sodium hypochlorite solution (35 c.c. containing 10% of available chlorine) and 30% sodium hydroxide solution (20 c.c.). Addition of sodium chloride (40 g.) gave a solid which on crystallisation from alcohol proved to be the original salt. Evaporation of the mother-liquor gave a small amount of a sodium salt, which gave an intense violet colour with zinc dust and alkali. The *p*-toluidine salt had m. p. *ca.* 285° (decomp.). The *sulphonyl chloride* had m. p. 212—215° (Found : C, 39·1; H, 3·0. $C_{18}H_{16}O_{10}N_2Cl_2S_2$ requires C, 39·0; H, 2·9%).

(*b*) Sodium hydroxide (20 g. in 20 c.c. of water) was added (20 mins.) to the sodium salt (14 g.) in sodium hypochlorite solution (300 c.c. containing 5% of available chlorine) at 85°. The red solution was cooled and left for 48 hours. The solid precipitate, which yielded a p-*toluidine* salt forming needles, decomp. 310—311°, from water (Found : C, 52·7; H, 5·0. $C_{18}H_{18}O_{12}N_2S_2,2C_7H_9N$ requires C, 52·5; H, 4·9%), was dissolved in water and treated with iron and hydrochloric acid at 100° (2 hours); the resulting precipitate was collected and extracted with dilute carbonate solution. Acidification of the extract gave a cream-coloured *solid*, which was crystallised from water but did not melt below 350° (Found : C, 43·6; H, 5·3. $C_{18}H_{22}O_8N_2S_2,2H_2O$ requires C, 43·7; H, 5·3%). It gave a sodium salt sparingly soluble in alkali or carbonate solutions.

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