338. *Cumyl Alcohol.*

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Cumyl (4-*iso*propylbenzyl) alcohol can be prepared in 42% yield by the cross Cannizzaro reaction on cuminal (4-*iso*propylbenzaldehyde) and formaldehyde. A more convenient preparation, yielding upwards of 70% of the pure alcohol, consists in the pressure hydrogenation of cuminal in the presence of copper–barium–chromium oxide catalyst.

Cumyl alcohol is characterised by its phenylurethane and *α-naphthylurethane*, the p-*nitro-* and 3 : 5-*dinitro-benzoates*, and its *hydrogen phthalate*, all of which are crystalline.

Previous work on cumyl alcohol was done by Kraut (*Annalen*, 1854, **92**, 66), Fileti (*Gazzetta*, 1884, **14**, 498), Law (J., 1907, **91**, 760), Palfray, Sabetay, and Mastagli (*Compt. rend.*, 1936, **203**, 1523), and Bert (*Bull. Soc. chim.*, 1925, **37**, 1252, 1577). The last-named author obtained it in 53—60% yield by passing a rapid stream of oxygen into an ethereal suspension of cumylmagnesium chloride. The only crystalline derivative we have been able to trace in the literature is the phenylurethane (Palfray, Sabetay, and Mastagli, *loc. cit.*). It was desired to have more extensive characterisation available for the identification of the alcohol as a constituent of essential oils, and so other methods of preparation were examined. The alcohol can be obtained in approximately 42% yield by the cross Cannizzaro reaction, but the most convenient method of all is the pressure hydrogenation of cuminal in the presence of copper–barium–chromium oxide catalyst. This yields upwards of 70% of pure redistilled cumyl alcohol, b. p. 91°/0·7 mm., $n_D^{20°}$ 1·5181. The alcohol is readily characterised by means of the derivatives named in the summary.

Experimental.

Preparation of Cumyl Alcohol.—Cuminal was isolated from *E. cneorifolia* oil and purified by the usual treatment of the bisulphite compound. It was optically inactive.

(a) *Cross Cannizzaro reaction.* A mixture of cuminal (50 c.c.; 0·3 mol.), methanol (70 c.c.), and 40% formaldehyde solution (80 c.c.; 1 mol.) was kept at 65—75° in a 2-l. flask (fitted with a dropping-funnel, reflux condenser, and mercury-sealed stirrer) during the slow addition, with constant stirring, of 50% sodium hydroxide solution (80 c.c.; 1 mol.), and for 40 minutes thereafter. The mixture was finally refluxed for 20 minutes and, on cooling, diluted with water (100 c.c.). The separated oil was drawn off, and the residue extracted four times with benzene (50 c.c. lots). Removal of the solvent from the washed and dried (anhydrous magnesium sulphate) oil and extracts, left an oil, which was distilled. The combined products from four experiments (180 c.c. of cuminal) were shaken for ½ hour with hot 35% sodium bisulphite solution (500 c.c.) and kept overnight. The unabsorbed oil was recovered by filtration and by washing of the bisulphite cake with ether; after washing with water, drying, and removal of the ether the residue was fractionated, pure cumyl alcohol (48 c.c.), $n_D^{20°}$ 1·5191, being collected at 109—110°/3·4 mm. The bisulphite cake (112 g.) was equivalent to 65 c.c. of cuminal, and the yield of alcohol was thus some 42% of the cuminal reacted upon.

(b) *The catalytic reduction of cuminal.* In a typical experiment, cuminal (50 g.) in ethanol (80 c.c.) containing copper–barium–chromium oxide (*J. Amer. Chem. Soc.*, 1932, **54**, 1138) (6 g.) was placed in a bomb with hydrogen (1340 lb. pressure), and the temperature raised to 120°. The pressure of hydrogen (1700 lb.) quickly fell when shaking was commenced, and after 2 hours had decreased to 1380 lb. The fall thereafter was slow and absorption was practically complete after a further hour (1240 lb.). On cooling, the liquid was filtered and poured into water, and the product recovered by steam-distillation. An ethereal extract of the distillate was shaken for several hours with sodium bisulphite solution to remove unchanged aldehyde (traces only). After filtration, washing with dilute sodium carbonate solution and water, and drying (anhydrous magnesium sulphate) the product was distilled, pure cumyl alcohol (36 g.), $n_D^{20°}$ 1·5181, being collected at 91°/0·7 mm.

Derivatives of Cumyl Alcohol.—The phenylurethane was prepared from cumyl alcohol and phenyl *iso*cyanate. After extraction with light petroleum (b. p. 60—90°) and filtration from some diphenylurea the phenylurethane crystallised in needles. Recrystallisation from the same solvent gave flat needles, m. p. 62° (Found: C, 75·7; H, 7·05; N, 5·15. Calc. for $C_{17}H_{19}O_2N$: C, 75·8; H, 7·1; N, 5·2%).

The α-*naphthylurethane*, similarly prepared (after a few minutes' gentle heating) and purified, crystallised from 90% spirit in long white needles, m. p. 112—112·5° (Found : C, 78·95; H, 6·8; N, 4·5. $C_{21}H_{21}O_2N$ requires C, 79·0; H, 6·6; N, 4·4%).

The p-*nitrobenzoate* was obtained from cumyl alcohol (5 g.), pyridine (5 c.c.), and *p*-nitrobenzoyl chloride (5·5 g.) by trituration in a warm mortar. After 2 hours, it was washed with ice-cold dilute sulphuric acid, water, 5% sodium carbonate solution, and water, submitted to steam-distillation to remove traces of the alcohol, dried, and thrice crystallised from methanol in a refrigerator, stout, pale yellow, prismatic needles, m. p. 39—39·5°, being obtained (Found : C, 68·0; H, 5·8; N, 4·75. $C_{17}H_{17}O_4N$ requires C, 68·2; H, 5·7; N, 4·7%).

The 3 : 5-*dinitrobenzoate*, prepared from cumyl alcohol (7 g.), pyridine (7 c.c.), and 3 : 5-dinitrobenzoyl chloride (9·5 g.), crystallised from methanol in long, fine, brittle, white needles somewhat resembling glass wool, m. p. 107° (Found : C, 59·4; H, 4·7; N, 8·15. $C_{17}H_{16}O_6N_2$ requires C, 59·3; H, 4·7; N, 8·15%).

The *hydrogen phthalate* was prepared by heating cumyl alcohol (10 g.) for 15 hours with phthalic anhydride (11 g.) in a loosely corked flask at 115°. The hot mixture was poured into excess of 5% sodium carbonate solution, and after filtration was left in the refrigerator until the sodium salt crystallised. The salt was washed with 5% sodium carbonate solution, and then dissolved in water and set aside in the refrigerator with an equal volume of the sodium carbonate solution. The crystals were again collected, and the process repeated. The salt was decomposed with dilute hydrochloric acid, the liberated oil extracted with chloroform, and the solvent evaporated after being dried with anhydrous magnesium sulphate. The syrupy phthalate solidified on nucleation with a crystal obtained from a previous preparation on long standing, and was twice recrystallised in the refrigerator from light petroleum (b. p. 60—90°) containing benzene (10%), solution being effected below 45°. Large needle-shaped plates, m. p. 61—62°, were obtained (Found : C, 72·3; H, 6·2. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·1%).

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[*Received, September 20th,* 1938.]