144. *Some Reactions of* o-*Hydroxybenzylacetone.*

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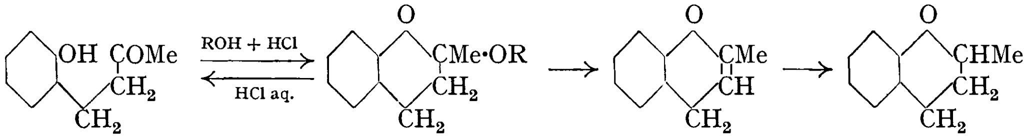
The reduction of *o*-hydroxybenzylideneacetone with sodium amalgam (Harries, *Ber.*, 1891, **24**, 3180; Harries and Busse, *Ber.*, 1895, **28**, 501) gives *o*-hydroxybenzylacetone (I). The same substance has also been prepared by catalytic reduction in presence of platinum-black (50% yield) (Nomura and Nozawa, *Sci. Rep. Tohuku Imp. Univ.*, 1918, **7**, 85), and in presence of a palladised strontium carbonate catalyst (80% yield) (this paper).

Catalytic reduction of *o*-hydroxybenzylideneacetone in methyl- or ethyl-alcoholic solution in presence of palladium chloride gave a mixture of (I) and (II; R = Me or Et), separated by dissolving the former in aqueous sodium hydroxide. This ready formation of six-membered cyclic acetals is closely analogous to the production of the methylglycosides



(I.) (II.) (III.) (IV.)

of the sugars, and is probably the first example of its kind in the aromatic series. In the purely aliphatic series Bergmann and Miekeley (*Ber.*, 1922, **55**, 1390) have shown that δ-acetyl-*n*-butyl alcohol gives a cyclic acetal with methyl alcohol and hydrogen chloride at room temperature. The formation of (II) is to be attributed to the presence of hydrogen chloride arising from the reduction of the palladium chloride; this is evident from the results obtained with the metallic platinum catalyst (Nomura and Nozawa, *loc. cit.*) and with the palladised strontium carbonate catalyst. 2-*Ethoxy*-2-*methylchroman* (II; R = Et) is readily prepared from (I) by the action of hydrogen chloride in ethyl alcohol, and is easily reconverted into (I) by heating with dilute hydrochloric acid; it is completely stable towards hot alkaline solutions.

o-Hydroxybenzylacetone (I), kept in ethereal solution over anhydrous sodium sulphate for two weeks, was converted into 2-*methylchromene* (III), probably through the intermediate (II; R = H). (III) was also obtained by boiling (II; R = Et) with acetic anhydride. Catalytic reduction of (III) gave 2-*methylchroman* (IV) as the sole product; reduction of the aromatic nucleus could not be effected.

2-Methylchroman is described in the literature, but it is very doubtful if it has previously been obtained in anything approaching a state of purity. Harries and Busse (*loc. cit.*) treated (I) in alcoholic solution with zinc dust and hydrochloric acid, and obtained a liquid, b. p. 223—226°/762 mm., with a coumarin-like odour, the analyses of which did not agree well with the formula (IV) and indicated an appreciable alteration during distillation. Compounds (II; R = Me and Et) actually have odours recalling that of peppermint, whereas both (III) and (IV) have an unpleasant " hydrocarbon " odour resembling that of naphthalene. We are of the opinion that Harries and Busse's product was a mixture containing a large amount of (II; R = Et) accompanied by (III) and (IV), a view which is confirmed by a comparison of the relevant boiling points. The product, b. p. 223°, prepared by Stoermer and Schäffer (*Ber.*, 1903, **36**, 2863) had an odour of peppermint and coumarin; it also is probably not 2-methylchroman. Borsche and Geyer (*Ber.*, 1914, **47**, 1154) have described the preparation of " 2-methylchromane " from (I) and zinc chloride, but the compound, b. p. 225°, was not examined or analysed.

EXPERIMENTAL.

o-*Hydroxybenzylacetone* (I).—*o*-Hydroxybenzylideneacetone (30 g.) (Harries, *loc. cit.*) in methyl alcohol (180 c.c.) and a 2% palladised strontium carbonate catalyst (12 g.) were shaken in hydrogen at 3 atmospheres until the required absorption had taken place, the time varying with different specimens of catalyst. The reaction mixture was filtered and fractionated; *o*-hydroxybenzylacetone (24 g.; 80% yield) distilled as a colourless viscous oil at 167—170°/16 mm. (Nomura and Nozawa, *loc. cit.*, give b. p. 160—167°/14·5 mm.). No product distilled below 145°/16 mm. Towards the end of the distillation the oil on the walls of the Claisen flask developed a violet colour (see below).

2-*Ethoxy*-2-*methylchroman* (II; R = Et).—(A) *o*-Hydroxybenzylideneacetone (16 g.) in ethyl alcohol (75 c.c.) was reduced by hydrogen in presence of palladium chloride (0·5 g.), the absorption being complete in 5 hours. The solution was filtered, diluted with aqueous sodium hydroxide, and extracted with ether and the extracts were shaken with dilute aqueous sodium hydroxide, dried over sodium sulphate, and distilled, leaving an almost colourless, mobile liquid (10 g.; 53% yield), b. p. 105°/11 mm. (Found: C, 74·6; H, 8·2. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The *chroman* has a rather faint odour of peppermint, and tends to acquire a pink tint on keeping; $n_D^{14.5°}$ 1·513. When distilled under ordinary pressure, b. p. 225°/760 mm., it acquires the odour of the chromene (III), and the rise of the refractive index also indicates a partial conversion into this compound. The alkaline solutions (above) were acidified, and yielded to ether *o*-hydroxybenzylacetone (I) (6·2 g.; 40% yield). (B) *o*-Hydroxybenzylacetone (7 g.) in ethyl alcohol (30 c.c.) containing a trace of hydrogen chloride was kept at room temperature for 16 hours, refluxed for 2 hours, and added to a large excess of sodium hydroxide solution (5%). The oil was extracted with ether, dried, and distilled, b. p. 110—111°/17 mm. (6·2 g.), $n_D^{16°}$ 1·512.

2-*Methoxy*-2-*methylchroman* (II; R = Me).—*o*-Hydroxybenzylideneacetone (10 g.) was reduced in methyl alcohol under the conditions described above. There were isolated *o*-hydroxybenzylacetone (3·9 g.) and an alkali-insoluble liquid (5·3 g.), b. p. 107°/14 mm. (Found : C, 74·7; H, 8·1. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·8%). The first few drops of the distillate had the odour of the chromene (III); this fact, and the analytical figures, indicated that the substance is probably not completely stable towards distillation. It had an odour very similar to that of the ethoxy-derivative, but rather more sharp; $n_D^{14°}$ 1·523.

2-*Methylchromene* (III).—(A) A specimen of *o*-hydroxybenzylacetone was preserved for 2 weeks in ethereal solution over anhydrous sodium sulphate. The product distilled at 95—97°/10 mm. as a colourless mobile oil with an odour recalling that of naphthalene; $n_D^{12°}$ 1·551 (Found : C, 82·3; H, 6·9. $C_{10}H_{10}O$ requires C, 82·2; H, 6·8%). When it was treated with an oxidising agent (chloranil) in presence of concentrated hydrochloric acid, an intense purple colour was developed [see preparation of (I), above]. (B) Compound (II; R = Et) was boiled with twice its weight of acetic anhydride for 2 hours, and then heated with water. An ethereal extract was shaken with sodium bicarbonate solution, dried, and distilled, yielding a colourless liquid, b. p. 95°/11 mm., having all the properties of that prepared under (A).

2-*Methylchroman* (IV).—2-Methylchromene (1·2 g.) in pure glacial acetic acid (12 c.c.) was shaken in hydrogen under slightly more than atmospheric pressure with a platinum–silica gel catalyst (0·5 g.; No. 17 of the Membranfilter Gesellschaft). Absorption of 1 mol. of hydrogen was complete in 4 hours, and no further absorption took place. The liquid was filtered, poured into water, and extracted with ether. The ethereal solution was washed thoroughly with sodium carbonate solution, dried, and fractionated under diminished pressure. 2-*Methylchroman* (0·9 g.) was obtained, b. p. 100—102°/11 mm., as a colourless mobile oil with an odour resembling that of the unsaturated compound; $n_D^{13·5°}$ 1·532 (Found : C, 80·9; H, 8·2. $C_{10}H_{12}O_2$ requires C, 81·1; H, 8·1%).

An attempt to reduce 2-methylchromene to the fully saturated octahydro-compound, 2-methylhexahydrochroman, with Adams's platinum oxide catalyst proceeded only to the chroman stage.

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