

## NOTES.

*p*-Dimethylaminobenzylidene Pentaerythritol. By ARTHUR FAIRBOURNE and JAMES WILLIAM WOODLEY.

IN the course of work on partly substituted polyhydric alcohols (J., 1921, 119, 1035, 2077; 1925, 127, 2759) *p*-dimethylaminobenzylidene pentaerythritol was isolated, and its further condensations investigated. The only previously recorded synthesis of a partly substituted pentaerythritol of this type was effected photochemically (Tanasescu, *Bul. Soc. Stiinte Cluj.*, 1923, ii, 111).

Aldehydes usually condense with pentaerythritol to produce the dialkylidene compounds (Read, J., 1912, 101, 2090), and *p*-dimethylaminobenzaldehyde has itself been recorded as acting in this way (Radulescu and Tanasescu, *Bul. Soc. Stiinte Cluj.*, 1922, i, 192).

On repeating the condensation, however, a different material was obtained when the crude product was crystallised from chloroform, instead of from acetone as recommended. Further investigation showed that the crude product from the Radulescu reaction always contained both mono- and bis-dimethylaminobenzylidene pentaerythritol, whatever strength of sulphuric acid between 10% and 60% was used, the best yield of the bis-compound being obtained with 10% and the best yield (almost quantitative) of the mono with 50%. They could be separated well by fractional crystallisation.

*p*-Dimethylaminobenzaldehyde and pentaerythritol in equal molecular proportions were thoroughly shaken with warm 50% sulphuric acid and after 12 hours the solution was treated with excess of dilute ammonia. The white precipitate obtained was dried on porous porcelain. Crystallisation from chloroform produced long, white needles of *p*-dimethylaminobenzylidene pentaerythritol,  $(\text{CH}_2\cdot\text{OH})_2\text{C} \begin{smallmatrix} \text{CH}_2\cdot\text{O} \\ \text{CH}_2\cdot\text{O} \end{smallmatrix} > \text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , m. p. 140° (decomp.),

or very indefinite at about  $180^\circ$  if the specimen had previously been kept at  $100^\circ$  for some hours (Found: C, 62.2; H, 8.2; N, 5.4.  $C_{14}H_{21}O_4N$  requires C, 62.9; H, 7.9; N, 5.2%).

In view of this very indefinite melting point, the identity of the substance was confirmed by preparing the methiodide and comparing this with the monomethiodide of bisdimethylaminobenzylidene pentaerythritol and also with that of dimethylaminobenzaldehyde itself, these three methiodides being prepared by heating the respective amines with excess of methyl iodide in sealed tubes for 2 hours at  $80-90^\circ$ , removing the excess of methyl iodide by evaporation from a bath at  $70^\circ$ , and recrystallising the products from alcohol in the case of *p*-dimethylaminobenzylidene pentaerythritol and from ether in the other two cases. The *methiodide* from *p*-dimethylaminobenzylidene pentaerythritol melted and decomposed at  $175^\circ$  (Found: I, 30.8.  $C_{15}H_{24}O_4NI$  requires I, 31.0%), that from bis-*p*-dimethylaminobenzylidene pentaerythritol at  $220^\circ$  (Found: I, 22.8.  $C_{24}H_{33}O_4N_2I$  requires I, 23.0%), and that from *p*-dimethylaminobenzaldehyde at  $160^\circ$  (Found: I, 43.3.  $C_{10}H_{14}ONI$  requires I, 43.6%).

The structure of *p*-dimethylaminobenzylidene pentaerythritol was also established by condensing the compound with a second molecule of *p*-dimethylaminobenzaldehyde and identifying the product with bis-*p*-dimethylaminobenzylidene pentaerythritol by the method of mixed melting point.

Attempts to prepare "mixed" spirans by condensing *p*-dimethylaminobenzylidene pentaerythritol with a molecule of a different aldehyde, *e.g.*, benzaldehyde or cinnamaldehyde, led to the elimination of the *p*-dimethylaminobenzylidene radical and the formation of spirans,  $CHR<\begin{smallmatrix} O\cdot CH_2 \\ O\cdot CH_2 \end{smallmatrix}>C<\begin{smallmatrix} CH_2\cdot O \\ CH_2\cdot O \end{smallmatrix}>CHR$ , identical (proved by the melting points of mixtures) with those obtained by direct condensation of the respective aldehydes with free pentaerythritol, thus indicating that aldehydic condensations of pentaerythritol are reversible (equilibrium) reactions.

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5-Methoxy- $\alpha$ -naphthaldehyde. By JOHN BALDWIN SHOESMITH and HANNES RUBLI.

5-METHOXY- $\alpha$ -NAPHTHALDEHYDE has been prepared by the catalytic reduction of 5-methoxy- $\alpha$ -naphthoyl chloride as follows:  $\alpha$ -Naph-

thylamine-5-sulphonic acid was converted into 1-cyanonaphthalene-5-sulphonic acid by the method of Royle and Schedler (J., 1923, 123, 1643) and then, by the addition of the calculated quantity of potassium carbonate, into the corresponding potassium salt, which (25 g. in small quantities at a time) was slowly added to a vigorously stirred, fused mixture of 250 g. of sodium hydroxide and 50 g. of water at a temperature which was allowed to rise slowly from 180° to 230° (compare D.R.-P. 413836). The mass, which finally became solid, was cooled and 5-hydroxy- $\alpha$ -naphthoic acid was liberated from an aqueous solution of it by addition of concentrated hydrochloric acid; after recrystallisation from dilute alcohol the acid melted at 235°. The acid (20 g.), dissolved in a solution of 15 g. of potassium hydroxide in 280 c.c. of water, was vigorously stirred with 15 g. of methyl sulphate at 40° for about 1 hour, and the alkaline solution was filtered and acidified. The 5-methoxy- $\alpha$ -naphthoic acid so precipitated was obtained free from the corresponding hydroxy-acid by allowing it to stand in an alkaline solution of diazotised sulphanilic acid for a day, after which the solution was acidified and the precipitate was dried carefully and extracted with dry benzene. The methoxy-acid of m. p. 228° (compare Fuson, *J. Amer. Chem. Soc.*, 1924, 46, 2787) had to be quite free from the hydroxy-acid before conversion into the acid chloride. The acid was dissolved in the calculated quantity of 20% alcoholic potassium hydroxide, and the solution evaporated to dryness. The dried potassium salt (10 g.) was added to a large excess of vigorously stirred thionyl chloride (18 c.c.) in dry benzene (18 c.c.). The whole was finally heated on the water-bath for about 5 minutes, cooled, and filtered from precipitated potassium chloride and acid, and the benzene and thionyl chloride were evaporated under reduced pressure. The residual 5-methoxy- $\alpha$ -naphthoyl chloride was distilled under reduced pressure. It had b. p. 194°/11 mm., and m. p. 80–81° (Found: Cl, 15.7.  $C_{12}H_9OCl$  requires Cl, 16.1%).

*5-Methoxy- $\alpha$ -naphthaldehyde.*—5-Methoxy- $\alpha$ -naphthoyl chloride (5 g.) in xylene (25 c.c.) in contact with palladinised barium sulphate was reduced by a current of dry hydrogen for 4 hours, the temperature of the bath being 170° (compare Rosenmund, *Ber.*, 1918, 51, 591). The aldehyde was separated in the usual manner as the bisulphite compound. It crystallised from light petroleum in light yellow plates, m. p. 66° (Found: C, 77.45; H, 5.5.  $C_{12}H_{10}O_2$  requires C, 77.45; H, 5.4%). The *p*-nitrophenylhydrazones forms red needles, m. p. 246°, from dilute acetic acid, the *semicarbazone* fine needles, m. p. 246°, from dilute acetic acid, and the *oxime* needles, m. p. 104°, from water or aqueous alcohol.

$\alpha$ -Naphthol,  $\beta$ -naphthol, and their methyl ethers were submitted

to the action of hydrogen in a similar manner, but no change was observed.

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*Some New Organo-tin Compounds.* By KENNETH KNIGHT LAW.

MANY unsuccessful attempts have been made to improve the yield of tribenzylstannic chloride in the method used by Smith and Kipping (J., 1912, 101, 2557); with all proportions of magnesium benzyl chloride between  $2\frac{3}{4}$  and  $3\frac{1}{2}$  mols. the product contains dibenzylstannic chloride, dibenzyl, a small proportion of hexabenzylstannane and probably also tetrabenzylstannane, although the last-named could not be obtained in a pure state.

*Hexabenzylstannane*,  $\text{Sn}(\text{C}_6\text{H}_5\cdot\text{CH}_2)_3\cdot\text{Sn}(\text{C}_6\text{H}_5\cdot\text{CH}_2)_3$ , is more conveniently prepared by heating tribenzylstannic chloride with sodium in toluene solution. It crystallises from acetone in colourless tablets, m. p.  $147\text{--}148^\circ$ , and is readily soluble in hot acetone or benzene (Found: Sn, 30.3.  $\text{C}_{42}\text{H}_{42}\text{Sn}_2$  requires Sn, 30.3%). It is readily decomposed by iodine in benzene solution, giving tribenzylstannic iodide.

*Dibenzylethylstannane*,  $\text{SnEtBu}(\text{CH}_2\text{Ph})_2$ , is prepared by treating dibenzylethylstannic iodide with excess of an ethereal solution of magnesium *n*-butyl bromide and completing the reaction by distilling the ether and heating the residue at about  $140^\circ$  during 1—2 hours. The product, isolated by fractional distillation, is a colourless, highly refractive liquid, b. p.  $207\text{--}209^\circ/9$  mm.,  $175\text{--}180^\circ/3\text{--}2.5$  mm. (Found: C, 61.4; H, 7.1.  $\text{C}_{20}\text{H}_{28}\text{Sn}$  requires C, 61.8; H, 7.2%). It is only moderately easily soluble in ether or acetone but more readily soluble in benzene.

*Benzylethylstannane*,  $\text{SnEtBu}_2\cdot\text{CH}_2\text{Ph}$ , was always obtained as a by-product in the above preparation, because the dibenzylethylstannic iodide invariably contained some benzylethylstannic iodide, which could not be removed by fractional distillation. The dibutyl compound is a colourless liquid, b. p.  $175\text{--}180^\circ/9$  mm.,  $118\text{--}122^\circ/2.5\text{--}3$  mm. (Found: C, 57.4; H, 8.7.  $\text{C}_{17}\text{H}_{30}\text{Sn}$  requires C, 57.7; H, 8.6%).

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