The Synthesis of Some 1,1,1-Trishydroxymethylalkanes

BENGT WEIBULL and MAGNUS MATELL

Research Laboratory, Mo och Domsjö AB, Örnsköldsvik, Sweden

The alkaline condensation of the lower aliphatic aldehydes with formaldehyde is a technically very important reaction. Here mention may be made only of the synthesis of pentaerythritol from acetaldehyde and formaldehyde [1]. The corresponding reaction with higher aldehydes has only met scant interest, presumably on account of the difficulty of obtaining these substances. The expected reaction products, 1,1,1-trishydroxymethylalkanes, might be of potential interest as raw materials for surface active agents (*cf.* Ref.[2]) and were synthesised as model compounds:

$$R{\cdot}CH_2CHO + 3\,HCHO + OH^- \longrightarrow$$
$$\rightarrow R{\cdot}C(CH_2OH)_3 + HCOO^-$$

The branched chain aldehyde, 2-ethylhexanal, was similarly condensed to 3,3-bishydroxymethylheptane. Table 1 summarises the results obtained.

Experimental. Octanal and 2-ethylhexanal were prepared in this laboratory by catalytic air oxidation of the corresponding alcohols. The other aldehydes were commercial products, obtained from Fluka A.G., Switzerland. All syntheses were made in much the same way. A typical experiment is described.

Undecanal (68 g; 0.4 mole) and aqueous formaldehyde (40 %; 224 g; 3 moles) were dissolved in 500 ml of aqueous ethanol (50 %; 500 ml). Potassium hydroxide (22.5 g; 0.4 mole) dissolved in 200 ml of 50 % aqueous ethanol was dropped into the solution with stirring and cooling. Following the addition of the alkali the mixture was stirred for 4 h at room temperature, then for 2 h at 50°. The ethanol was then evaporated and the inhomogeneous mixture extracted with ether. Evaporation of the ether yielded a residue that was distilled in vacuum. The main fraction (43 g; 47 %) had b.p./1 mm Hg 187–190°. It was further purified by recrystallisation from ligroin. M.p. 77–79.

In some experiments sodium hydroxide was used instead. The high proportion of formaldehyde is probably not necessary as some of the aldehydes were reacted with only the theoretical amount without appreciably inferior yield.

The authors are indebted to Mr. C. Engblom and Mr. C. E. Lindahl, who skilfully carried out most of the experimental part of this work.

1. Berlow, E., Barth, R. H. and Snow, J. E. *The Pentaerythritols*, Reinhold Publishing Co., New York 1958.
2. Oda, R. *Fette, Seifen, Anstrichmittel* **59** (1957) 921.
3. Dupont, G., Dulou, R. and Duplessis-Kergomard, A. *Bull. soc. chim. France* **1949** 314.
4. Dermer, O. C. and Solomon, P. W. *J. Am. Chem. Soc.* **76** (1954) 1697.
5. Shortridge, R. W., Craig, R. A., Greenlee, K. W., Derfer, J. M. and Boord, C. E. *J. Am. Chem. Soc.* **70** (1948) 946.

Received May 8, 1962.

Table 1. Properties of compounds $R.C(CH_2OH)_3$.

R	Yield %	B. p. °C/mm Hg	Cryst. from	M.p. °C	Found C	Found H	Found O	Calc. C	Calc. H	Calc. O
C_5H_{11}	61	160–162/1.5	CCl_4	64–65.5[a]	61.3	11.32	27.2	61.3	11.44	27.2
C_6H_{13}[b]	—	—	$CHCl_3$	68–70[c]	—	—	—			
C_8H_{17}	65	190–200/1.5	Ligroin	73.5–75[d]	66.3	11.90	22.1	66.0	12.00	22.0
C_9H_{19}	47	187–190/1	»	77–79	67.3	12.05	20.7	67.2	12.15	20.7
$C_{10}H_{21}$	45	180–186/0.3	»	79.5–81	68.1	12.11	19.6	68.2	12.27	19.5
$C_{12}H_{25}$	51	200–220/2.5	»	83–88	70.0	12.54	17.4	70.1	12.50	17.5
$C_9H_{20}O_2$[e]	83	136–143/8	—	40–42.5[f]	—	—	—			

[a] M.p.[3] 59
[b] Found: OH 26.5; calc.: OH 26.81.
[c] M.p.[4] 68–68.8
[d] M.p.[4] 72–73
[e] The compound is 3.3-bishydroxymethylheptane. Found: OH 21.2; calc.: OH 21.23.
[f] M.p.[5] 41.4–41.9