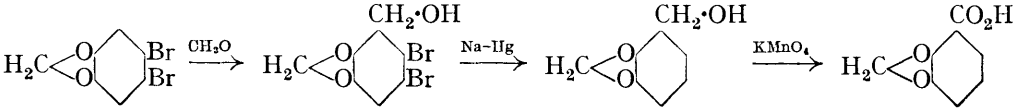
NOTES.

Derivatives of o-*Piperonal.* By THOMAS S. STEVENS.

PERKIN and TRIKOJUS (J., 1926, 2925) prepared some simple derivatives in this series from *o*-piperonylic acid (IV), derived ultimately from *o*-vanillin. Compounds of the same class can be obtained in moderate yield from dibromocatechol methylene ether (I) (Jones and Robinson, J., 1917, **111**, 913) as follows:



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

2 : 3-*Dibromo*-5 : 6-*methylenedioxybenzyl Alcohol* (II).—A mixture of acetic acid (250 c.c.), concentrated sulphuric acid (70 c.c.), and formalin (25 c.c. of 38%) was added to dibromocatechol methylene ether (30 g.) in hot chloroform (30 c.c.), and the whole kept at 40° for 2 weeks. It was diluted with water and extracted with chloroform, the extract washed with water and sodium carbonate solution, and the chloroform evaporated. The residue was heated for several hours with alcoholic potash to hydrolyse the acetyl derivative of (II), and unchanged (I) distilled in steam. The non-volatile resinous solid was extracted with hot 70—80% methyl alcohol; the extracts, boiled with charcoal and concentrated, yielded the *dibromo-alcohol*, which formed prisms from benzene, m. p. 115° (Found: Br, 51·5. $C_8H_6O_3Br_2$ requires Br, 51·6%).

o-*Piperonyl Alcohol* (2 : 3-*Methylenedioxybenzyl Alcohol*) (III).—The foregoing alcohol, in boiling 70% methyl alcohol (20 parts), was reduced with sodium amalgam (50—60 parts of 3%), most of the alkali formed being neutralised with acetic acid. The mixture was concentrated somewhat and extracted with ether, and the dried extract distilled. o-*Piperonyl alcohol*, b. p. 165°/30 mm., crystallised from benzene–ligroin in needles, m. p. 34—35° (Found : C, 63·2; H, 5·5. $C_8H_8O_3$ requires C, 63·2; H, 5·3%). It dissolved readily in benzene and sparingly in hot water; oxidised by aqueous permanganate, it yielded *o*-piperonylic acid, identical (mixed m. p.) with a specimen prepared according to Perkin and Trikojus. With hot, very dilute chromic acid mixture, it gave *o*-piperonal, identified as the *p*-nitrophenylhydrazone, which had the properties ascribed to it by the same authors.—THE UNIVERSITY, GLASGOW. [*Received, March* 21*st*, 1935.]

The Odd-membered n-*Primary Alcohols* (*The* $\alpha \longrightarrow \beta$ *Transition*). By THOMAS MALKIN.

IN a recent paper dealing with the dimorphism of certain aliphatic compounds (J., 1934, 1661, par. 3) Phillips and Mumford state that their results " show definitely " that the odd alcohols above C_{14} exist in a β-tilted form, and that Malkin's conclusions (*J. Amer. Chem. Soc.*, 1930, **52**, 3739), which indicate a vertical chain and are based on *X*-ray measurements, " would appear to be based on a misinterpretation."

It is not at all clear how Phillips and Mumford come to these conclusions, but it can be stated quite definitely that there is no evidence in support of their claim.

As is well known, the question of the tilt of the chain in solid long-chain compounds can only be decided by *X*-ray investigation; yet, notwithstanding the positive terms of their criticism, Phillips and Mumford do not adduce a single *X*-ray measurement. On the other hand, the *X*-ray results published in the above paper have been repeated, confirmed, and extended by Wilson and Ott (*J. Chem. Physics*, 1934, **2**, 231) and further extended and confirmed by Piper, Chibnall, and Williams (*Biochem. J.*, 1934, **28**, 2175). Thus, three independent investigations have established that the chains in odd alcohols are always vertical.

The evidence which Phillips and Mumford consider sufficient to refute this body of *X*-ray data is the observation that odd alcohols undergo an $\alpha \longrightarrow \beta$ transition, a few degrees below the melting point, and it is clear from the text that they are under the impression that the mere existence of a β-form is *proof* of a tilted chain. This view is, however, based on an erroneous assumption that all β-forms possess tilted chains. Müller has shown that the β-forms of odd paraffins possess vertical chains (*Proc. Roy. Soc.*, 1928, *A*, **120**, 437; 1930, *A*, **127**, 417; 1932, *A*, **138**, 514).

The correct explanation of the above $\alpha \longrightarrow \beta$ change was suggested several months prior to the publication of Phillips and Mumford's paper, by Wilson and Ott (*loc. cit.*), who stated that the transition is probably due to a change in the rotation of the molecules, not involving any change in length; *i.e.*, a change from a vertical rotating (α) form to a vertical non-rotating (β) form. Since, however, Wilson and Ott did not investigate the changes in side spacings which accompany changes in rotation (Müller, *Nature*, 1932, **129**, 436; *Proc. Roy. Soc.*, 1932, *A*, **138**, 514; see also Malkin, *Trans. Faraday Soc.*, 1933, **29**, 977), I have measured the side spacings of the α- and β-forms of C_{15}, C_{17}, and C_{19} alcohols and find, in agreement with the above suggestion, that the β-forms give two main spacings (3·7 and 4·2 Å.), whereas the α-forms give only one (4·2 Å.).

Further confirmation of rotation in the α-forms of odd alcohols is given by their optical properties. Thus, the α-forms of the above three alcohols are uniaxial, whereas the β-forms are biaxial. These results are in harmony with the observations of Bernal, who found the same difference between the α- and the β-form of the even alcohol, dodecylol (*Z. Krist.*, 1932, **83**, 153).—THE UNIVERSITY, BRISTOL. [*Received, March* 26*th*, 1935.]