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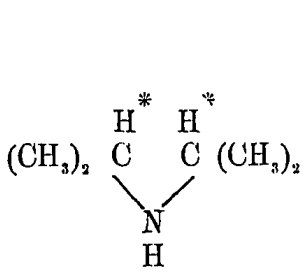
Chemistry. — *"On α α'-tetramethylpiperidine."* By Prof. A. P. N. FRANCHIMONT and Dr. H. FRIEDMANN.

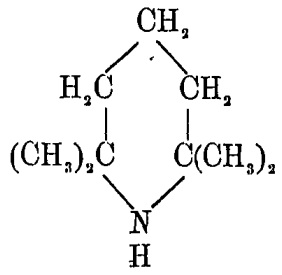
(Communicated in the meeting of September 24, 1904).

This substance, which was obtained in 1885 by CANZONERI and SPICA but in an impure condition, was prepared by us in another manner, namely, by reduction of γ-bromotetramethylpiperidine with a copper-zinc couple (Gladstone-Tribe's method) in absolute alcoholic solution.

It is a liquid boiling at 155,°5—156°5 at 760 m.m. pressure having a sp. gr. of 0.8367. With water it yields a crystalline compound which melts at 28° and loses its water totally or partially in a dry atmosphere. The compounds with hydrogen chloride, hydrogen bromide and sulphuric acid form very beautiful crystals; those with the two first-named acids sublime on heating without previous fusion, those with sulphuric acid melt: the acid one at 174°, the neutral one at 270°.

Compared with piperidine, this amine reacts remarkably slowly on acid chlorides such as benzoyl chloride, chloro-formic esters, picrylchloride etc. In aqueous solutions the reaction takes place hardly at all, in ethereal solutions extremely slowly. However, there were obtained: methylurethane as a liquid with a strong mint-like odour boiling at 227° at a pressure of 760 m.m.; sp. gr. 0.9848 and the benzoyl derivative as crystals melting at 41°—42°; the picryl derivative melts at 225°. An effort to prepare a urea from the hydrogen chloride compound and potassium isocyanate has resulted as yet in failure. This reminds us of experiments of Dr. K. H. VAN DER ZANDE in 1889 with di-isopropylamine, where urea could only be obtained with difficulty and in very small amount, whereas dinormalpropylamine presented no difficulties [1]). If we compare the formulae of di-isopropylamine and α α'-tetramethylpiperidine we notice that they only





[1]) Some years before, I had already noticed an analogous phenomenon when treating propyl- and isopropylmalonic acid with nitric acid; the first compound is much more readily attacked than the second.

differ in this way that the two hydrogen atoms of the first compound (indicated by asterisks) have been replaced in the second one by the bivalent group $CH_2—CH_2—CH_2$; piperidine and tetramethylpiperidine differ because the first one contains hydrogen atoms where the other possesses methyl groups, namely at the α C atoms in regard to the nitrogen.

As piperidine reacts strongly with the above substances and tetramethylpiperidine does not do so and as there exists an analogous difference between dinormalpropylamine and di-isopropylamine it is natural to look for the cause of this in the methyl groups. As, however, their nature does not explain this difference we are bound to consider their mass and their position in space in regard to the nitrogen. This is then a case of so-called sterical obstacle which is to a certain extent comparable with a number of other cases which have been chiefly observed in the aromatic compounds; a case which may, perhaps, affect the views held as to the nitrogen atom.

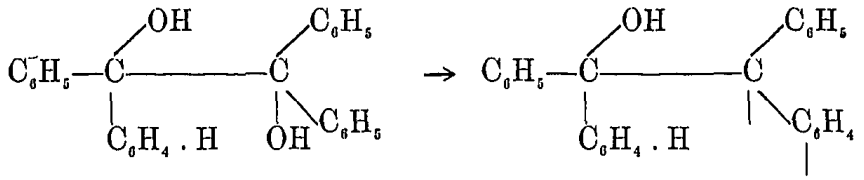
It must be finally observed that tetramethylpiperidine yields like di-isopropylamine a crystalline compound with nitrous acid, which is fairly stable and is only decomposed at a higher temperature into water and the nitroso-compound.

Chemistry. — "*On intramolecular atomic rearrangements in benzpinacones.*" By P. J. MONTAGNE. (Communicated by Prof. A. P. N. FRANCHIMONT).

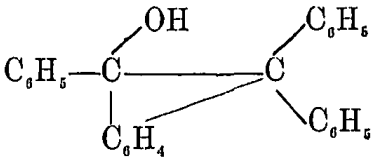
(Communicated in the meeting of September 24, 1904).

The following research originated in an effort by NEF[1]) to explain the intramolecular atomic rearrangement in the conversion of benzpinacone into benzpinacoline by assuming the presence of an intermediate product. His explanation when put into formulae is as follows:

Benzpinacone is dissociated into water and unsaturated hydrocarbon:



then addition to:



[1]) Ann. 318 p. 38.