

over 90% were obtained. Under the best conditions so far obtained almost 10% of the phenol was oxidized with consequent reduction of the nitric acid.

### Conclusions.

1. A survey of the literature showed that when metals dissolved in nitric acid, nitrous oxide was produced as well as higher oxides of nitrogen. In some cases the metallic salt acted as a catalyst in the production of nitrous oxide.

2. This reduction of nitric acid to nitrous oxide may also occur in organic nitrations. In the nitration of phenol to trinitrophenol by weak nitric acid as much as 25% of the nitric acid may be reduced to nitrous oxide and nitrogen. The presence of iron salts accelerated this reduction.

3. By keeping the temperature of nitration well below 100° especially in the initial stages the formation of nitrous oxide and nitrogen may be avoided, only higher oxides of nitrogen being produced.

4. It was not found possible to nitrate phenol without causing some reduction of the nitric acid to oxides of nitrogen. The best results were obtained by sulfonating phenol almost to the disulfonate stage with 96% sulfuric acid and then nitrating at low temperatures (30°-40°) with a mixture of sulfuric and nitric acid.

NEW YORK, N. Y.

---

[CONTRIBUTION FROM THE ORGANIC LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

## DIMETHYL-PROPYL-CARBINOL AND SOME OF ITS DERIVATIVES.

BY ANDRÉ DESCHAMPS.

Received October 8, 1920.

### Introduction.

Originally the object of this work was to carry out an idea of M. G. C. Chavanne<sup>1</sup> involving the preparation of trimethyl-propyl-methane. Since Markownikoff's method is both hazardous and expensive, I attempted to prepare the compound by the action of methyl magnesium iodide upon methyl-2-bromo-2-pentane.<sup>2</sup> This reaction also proving impracticable, I resorted to the investigation of dimethyl-propyl-carbinol, which I had obtained as an intermediate product in the preparation of the latter substance.

### Preparation of Dimethyl-propyl-carbinol.

This compound was prepared from both *n*-propyl iodide and *n*-propyl bromide by the Grignard reaction. The latter is better than that using ethylbutyrate described by Masson.<sup>3</sup>

<sup>1</sup> G. C. Chavanne, Professor of Chemistry at University of Brussels (Belgium).

<sup>2</sup> Markownikoff, *Monatsh.*, **34**, 1965 (1913).

<sup>3</sup> Masson, *Compt. rend.*, **1901**, pp. 132-484.

1. **From *n*-Propyl Iodide.**—19.4 g. of *n*-propyl-magnesium iodide was prepared as usual and after cooling to 0°, a mixture of 5.8 g. of acetone scrupulously dried, and an equal volume of anhydrous ether was added drop by drop. The reaction was very violent, and since the product was not entirely soluble, the whole was allowed to stand for 24 hours, as advised by Grignard in such cases. The next day the reaction product was poured upon a mixture of 9 g. of powdered ice and 9 g. of glacial acetic acid. After extraction with ether and suitable washings the distillation gave a principal fraction boiling at 110°–132°. The product obtained in this way was always contaminated by iodine compounds.

2. **From *n*-Propyl Bromide.**—14.7 g. of *n*-propyl-magnesium bromide and 5.8 g. of acetone were used in exactly the same manner as in the previous experiment. The course of the reaction was identical, except that in the end no trace of halogen could be discovered in the carbinol so prepared.<sup>1</sup> This was fractionated in a Hempel column, and the fraction boiling at 121°–124° was collected. The boiling point recorded by Beilstein is 122.5°–123.5° at 762 mm. Yield, 50%.

#### Properties of Dimethyl-propyl-carbinol.

Beilstein records no physical properties of dimethyl-propyl-carbinol except the boiling point. I found it a slightly viscous liquid, almost insoluble in water, soluble in alcohol and ether, and possessing an odor suggesting freshly peeled bark. It boils at 122.5°–123.5° at 762 mm.;  $d_{4.4}^{13.5}$  0.8350,  $n_{15.5}^{15.5}$  1.4125.

**Freezing-Point Determination.**—Crystallization was not effected at –20°. The carbinol was therefore immersed in liquid air at –193°, whereupon it became more and more viscous, and finally a solid, transparent mass, exhibiting no outward signs of crystalline structure. The freezing point was determined by the use of a potentiometer and suitable thermocouples. As the frozen substance was allowed to stand in the air a break in the curve occurred between –107° and –109°. This can be considered as the true melting point of dimethyl-propyl-carbinol, which therefore probably possesses a minute crystalline structure.

#### Methyl-2-Bromo-2-Pentane.

The best results were obtained when one mol of dimethyl-propyl-carbinol was boiled with 4 mols of hydrobromic acid (sp. gr. 1.45) for half an hour and then distilled. In the distillate the organic bromide forms a layer above the hydrobromic acid, but the behavior of the meniscus between the liquids is peculiar for it does not remain horizontal when the tube is inclined.

The bromide is so easily decomposed by pure water, that it is best, after separating the layers, to treat it directly with calcium chloride and then remove the hydrobromic acid by a current of air.

<sup>1</sup> Tested with metallic sodium.

Subs., 0.1000: AgBr, 0.1140.

Calc. for  $C_6H_{13}Br$ : Br, 48.48. Found: 48.51.

Methyl-2-bromo-2-pentane is not recorded in Beilstein, but N. Nynera<sup>1</sup> obtained it in small quantities by the bromination of dimethyl-cyclopropane. He found the methyl-2-bromo-2-pentane a mobile liquid, having a pleasant odor suggestive of turpentine. It did not freeze at  $-18^\circ$ ;  $n_D^{23}$  1.442;  $d_4^{23}$  1.117.

**Methyl-2-Chloro-2-Pentane.**—One mol of carbinol was treated with 4 mols of conc. hydrochloric acid (sp. gr. 1.20). Butlerow describes this compound<sup>2</sup> as boiling with decomposition at about  $100^\circ$ . It was therefore distilled under reduced pressure, and found to boil at  $50^\circ$  to  $53^\circ$  under 41 mm. pressure.

**Phenylurethane of Dimethyl-propyl-carbinol.**—When equivalent quantities of phenyl isocyanate and dimethyl-propyl-carbinol were mixed and boiled a few minutes, a reaction ensued producing a heavy precipitation of fine white crystals. These were insoluble in hot ether, water, benzene, cyclohexane, chloroform, and petroleum ether, and somewhat soluble in hot alcohol and acetone. Recrystallization from these 2 solvents gave beautiful, long, white needles melting at  $239^\circ$ .

Subs., 0.1075, 0.093: N, 67.7 cc. ( $28^\circ$ , 762 mm.), 57.2 cc. ( $28^\circ$ , 762 mm.).

Calc. for  $C_{13}H_{19}O_2N$ : N, 6.33. Found: 6.89, 6.73.

**Benzoate of Dimethyl-propyl-carbinol.**—This substance was prepared from benzoyl chloride by the Schotten-Baumann reaction<sup>3</sup> in pyridine solution. After dissolving the pyridine hydrochloride in diluted sulfuric acid, the oil was extracted with ether and we obtained on cooling a white body which was recrystallized from alcohol. It gave beautiful, white needles, melting at  $182-183^\circ$ . It was not analyzed.

### Summary.

1. Dimethyl-propyl-carbinol has been prepared with good yields by 2 new methods, and its physical and chemical properties investigated.
2. The following derivatives have also been prepared and studied: (a) methyl-2-bromo-2-pentane, (b) methyl-2-chloro-2-pentane, (c) the phenylurethane, (d) the benzoate.
3. Attempts to prepare trimethyl-propyl-methane by several methods proved unsuccessful.

The author wishes to express here his gratitude to Dr. F. J. Moore for many helpful suggestions.

CAMBRIDGE 39, MASS.

<sup>1</sup> Nynera, *J. Russ. Phys. Chem. Soc.*, 44, p. 178.

<sup>2</sup> *Bull. soc. chim.*, 5, 40 (1866).

<sup>3</sup> Lassar-Cohn, "Arbeitsmethoden für organisch-chemische Laboratorien," 1903, p. 224.