

$\alpha$ -Methylamyl iodide with piperidine in heptane forms a crystalline  $\alpha$ -methylamyl-piperidinium-iodide. This is considered to be analogous in structure to the piperidine-metalloid compounds described above.

Thanks are due to Professor Edward Kremers for guidance in this investigation.

MADISON, WISCONSIN.

---

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

### TETRAPROPYL-ETHANE.

BY JEAN PICCARD AND RAY Q. BREWSTER.<sup>1</sup>

Received August 9, 1921.

The number of heavier hydrocarbons with side-chained structures described in the literature is very small. Yet these hydrocarbons are of interest not only to the physical chemist in view of their surface tension and other constants, but also to the organic chemist for the identification of the carbon skeleton of unknown compounds. While in recent years many new methods have been found for the determination of characteristic groups in organic molecules, practically no progress has been made toward the determination of the carbon skeleton since Baeyer's distillation with zinc dust and its famous application to the identification of alizarin. So many good reducing agents have been found in the last few years, however, that it should be possible in most cases to reduce, in well defined successive steps, any organic compound to the corresponding saturated hydrocarbon.

Several years ago Baeyer and Piccard,<sup>2</sup> while working on dimethylpyrone, discovered an interesting violet dye of unknown constitution. The identification of its carbon skeleton was attempted by the oxidation methods in general use. A considerable number of new derivatives were thereby obtained without any progress toward the solution of the problem, since all the oxidation products obtained were unknown.

The problem was later attacked by Piccard and Edmond Wallach and still later by Piccard and McLauren, who applied successively different reduction methods with the purpose of obtaining a saturated hydrocarbon. Unfortunately this work was twice interrupted by the military obligations of the collaborators. Since there are reasons for believing that the hydrocarbon which would result from complete reduction of the violet dye would be symmetrical tetrapropyl-ethane, and since this hydrocarbon is not yet described in the chemical literature, the present work was begun parallel to the work of our collaborators Wallach and McLauren, with the

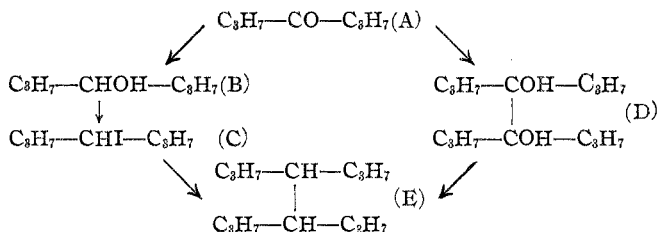
<sup>1</sup> The material presented here is used by Ray Q. Brewster in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

<sup>2</sup> Baeyer and Piccards, *Ann.*, **384**, 208 (1911); **408**, 332 (1915).

purpose of synthesizing the new hydrocarbon by the Wurtz reaction. Since the reduction of the violet dye has thus been indefinitely delayed this synthesis of tetrapropyl-ethane is now published separately.

### The Synthesis of Sym. Tetrapropyl-ethane.

The plan of the work was as follows. Butyrene (A) obtained by the dry distillation of calcium butyrate, was reduced by means of metallic sodium and a little water, forming as the chief product  $\delta$ -oxyheptane (B) and a smaller quantity of the pinacone, tetrapropyl-glycol (C). The  $\delta$ -oxyheptane (dipropyl-carbinol) was transformed into its iodide<sup>3</sup> (D) which, when boiled with sodium in ether solution, gave the desired hydrocarbon, tetrapropyl-ethane, (E). However, the fact that the Wurtz reaction is sometimes liable to proceed with rearrangements led us to look for another method for the synthesis of the tetrapropyl-ethane. For this purpose the reduction of the symmetrical tetrapropyl-glycol was selected.



The reduction of the pinacone was a difficult piece of work but there was finally obtained a pure hydrocarbon in quantities sufficient for comparison with the hydrocarbon first prepared from the  $\delta$ -heptyl iodide. Both compounds were found to be identical. Hence the new tetradecane is the desired *sym.* tetrapropyl-ethane or bis- $\delta$ -heptyl.

### Experimental Part.

Butyrene was prepared by the distillation of calcium butyrate. In the first experiments the calcium butyrate, in 200 to 300g. lots, was distilled from a large copper tube heated in a combustion furnace. However, there was some difficulty with the tube becoming clogged; and the yield of the butyrene was not so large as when the calcium butyrate was distilled in smaller portions. This observation is in agreement with the experiments of Chancel.<sup>4</sup>

In the method finally adopted the calcium butyrate was distilled from a 500cc. copper flask in portions of 50 g. each. Before beginning the operation the air was swept out of the flask by a stream of carbon dioxide. The carbon dioxide was then shut off and the flask heated with the full heat of one Bunsen burner. At the end of the process the volatile products remaining in the flask were carried over into the condenser by a stream of carbon dioxide. The average yield was about 26 cc. of crude butyrene

<sup>3</sup> Friedel, *Jahresber.*, 1869, 514.

Kurtz, *Ann.*, 161, 214 (1872).

<sup>4</sup> Chancel, *Ann.*, 52, 295 (1844).

with 2.5–3.0 cc. of water. The time used for the complete operation was about 25 minutes.

The crude butyrene (465 cc.) was subjected to a steam distillation, dried and fractionated. The fraction boiling at 140–146° was collected. Yield, 200, g. The moistened butyrene was reduced to dipropyl-carbinol and tetrapropyl-glycol by means of metallic sodium.<sup>5</sup> In order to increase the relative yield of the pinacone the butyrene was diluted with as little ether as possible. From 120 g. of butyrene there was obtained 84 g. of  $\delta$ -oxyheptane and 23.5 g. of the tetrapropyl-glycol, boiling at 150° and 260° respectively. The latter solidified in the receiver, and after recrystallization from ether melted at 68°.

$\delta$ -Heptyl iodide,  $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CHI}$ .—Fifty g. of  $\delta$ -oxyheptane (dipropyl-carbinol) was mixed with 10 g. of red phosphorus and to this was added 60 g. of iodine in small portions. After 3 hours the reaction product was washed with dil. sodium hydroxide solution, dried and distilled. It passed over with partial decomposition at 180–185°. Distillation under reduced pressure gave the heptyl iodide in almost colorless form. It distils at 65–67° under 9 mm. pressure with only very slight decomposition.<sup>6</sup>

*Analyses.* Subs., 0.1322, 0.2245: AgI, 0.1363, 0.2323. Calc. for  $\text{C}_7\text{H}_{15}\text{I}$ : I, 56.19. Found: 55.73, 55.93.

*Sym. Tetrapropyl-ethane*,  $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CHCH}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$ .—For the preparation of symmetrical tetrapropyl-ethane by the Wurtz reaction, 58 g. of  $\delta$ -heptyl iodide was dissolved in 150 cc. of absolute ether. Twenty g. of sodium wire was added and the solution was boiled for 20 hours. The ether solution was then separated from the sodium iodide and unchanged sodium, washed with water and dried. After removal of the ether the remaining oil was fractionated. The first portion of the distillate consisted of 8 cc. of a hydrocarbon boiling at 98–100° which undoubtedly was *n*-heptane. The main fraction distilled at 215–225° and was considered to be the desired tetrapropyl-ethane. After purification with conc. sulfuric acid and redistillation the product gave the boiling points 220° at 760 mm. and 105–106° at 12 mm. It was halogen-free (copper oxide test), and the pink coloration produced by a trace of iodine showed that it was also free from oxygen. The liquid is remarkably thin for a hydrocarbon of such a high molecular weight. This low viscosity is due to the fact that the molecule contains two side chains. On cooling with solid carbon dioxide and ether the oil became extremely viscous but did not crystallize.

The combustion was made in an atmosphere of nitrogen.

*Analyses.* Subs., 0.1200, 0.1383:  $\text{CO}_2$ , 0.3730, 0.4297;  $\text{H}_2\text{O}$ , 0.1630, 0.1912. Calc. for  $\text{C}_{14}\text{H}_{30}$ : C, 84.75; H, 15.25. Found: C, 84.77, 84.74; H, 15.20, 15.47.

The molecular weight was measured by the freezing-point method in benzene solution.

*Analyses.* Wt. of benzene, 16.22 g. Subs., 0.0812, 0.1984, 0.3367: depression, 0.129°, 0.327°, 0.539°. Mol. wt., calc.: 198. Found: 198.6, 187.5, 192.5; mean, 193.

Measurements of the density, the surface tension and the index of refraction were also made. These constants will be given together with the constants of the hydrocarbon prepared from tetrapropyl-glycol.

#### Preparation of Tetrapropyl-ethane from Tetrapropyl-glycol.

Three g. of tetrapropyl-glycol was reduced to the parent hydrocarbon by being heated at 180° in a sealed tube with 15 cc. of conc. hydriodic acid for 10 hours. The

<sup>5</sup> Kurtz, Ref. 3.

<sup>6</sup> Kurtz, Ref. 3, did not obtain the iodide in pure condition. He reported only 47.72% of iodine in his product.

reaction mixture of 6 combined lots was treated with sodium hydroxide and the remaining oil taken up with ether. The ether solution was washed with water and dried. After removal of the ether the main fraction distilled at 210–230°. The formation of free iodine and hydriodic acid showed that the product still contained some iodide. Another treatment with hydriodic acid removed all but traces of iodine. This last small amount was removed with zinc dust, acetic acid and alcohol.<sup>7</sup> The product thus obtained was halogen-free but with iodine it gave a brown color indicating the presence of an oxygen-containing compound. For the removal of this the oil was shaken with pure conc. sulfuric acid, separated and distilled over sodium. There was then obtained about 7 cc. of pure hydrocarbon which boiled at 220°. It gave a pink color with iodine and did not decolorize a very dilute solution of potassium permanganate. At a pressure of about 12 mm. of mercury it boiled at 107°. The hydrocarbon is a very thin liquid, which on cooling with solid carbon dioxide and ether became quite viscous but did not crystallize.

*Analyses.* Subs., 0.1187, 0.1502: CO<sub>2</sub>, 0.3690, 0.4680; H<sub>2</sub>O, 0.1610, 0.2045. Calc. for C<sub>14</sub>H<sub>30</sub>: C, 84.75; H, 15.25. Found: C, 84.79, 84.98; H, 15.18, 15.24.

The molecular weight was measured by the freezing-point method in benzene solution.

*Analyses.* Wt. of benzene, 16.27 g. Subs., 0.0944, 0.2137, 0.3919: depression, 0.149°, 0.333°, 0.617°. Mol. wt., calc.: 198. Found: 194, 197, 195; mean, 195.

The physical constants were measured under the same conditions under which they had been measured for the hydrocarbon prepared by the Wurtz reaction. The following table shows the identity of both hydrocarbons. The slight differences may be accounted for by traces of impurities that might be produced in either process. We assume that the hydrocarbon produced by the Wurtz reaction is the purer.

	Prepared by the	
	Wurtz Reaction.	Reduction of Pinacone.
B. p. at atm. pressure.....	220°	220°
B. p. at 12 mm.....	105–106°	107°
Density, 25°.....	0.7735	0.7749
Surface tension (measured with a Traube stalagmometer).....	25.64	25.31 dynes/cm.
Index of refraction (Abbe refractometer) at 25°.....	1.4322	1.4335
Consistency at room temperature....	very liquid	very liquid
Consistency at –80°.....	very viscous	very viscous.

### Summary.

Sym. tetrapropyl-ethane has been prepared by two synthetic methods and its physical properties measured. These data will be of value in further work on the reduction products of dimethyl-pyrone.

CHICAGO, ILLINOIS.

<sup>7</sup> Wislicenius, *Ann.*, 219, 312 (1883).