92. *Higher Aliphatic Compounds. Part III. The Preparation of Paraffins.*

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Methods hitherto available for the preparation of paraffins from the halides have been unsatisfactory. For example, that of Levene, West, and van der Scheer (*J. Biol. Chem.*, **1915**, **20**, 523) involves a lengthy reduction of the iodide in acetic–hydrochloric acid *suspension* with zinc dust. The reaction is slow and often incomplete, because (*a*) little of the iodide is in solution and (*b*) the unreactive alkyl chloride may be formed by double decomposition.

The three methods now recommended give good yields of the pure products and make the paraffins easily available.

Method (*i*).—To a boiling solution of cetyl (hexadecyl) iodide (m. p. 22°) (11 g.) in AcOH (250 c.c.), Zn dust was added in 3 portions during 3 hr. The liquid was decanted from the unchanged Zn, ice-water (150 c.c.) added, and the cetane collected and washed. It was free from iodine. Yield (dry), 6·7 g. (95%); m. p. 17°. Pure cetyl iodide (f. p. 23·3°) (22 g.) was similarly reduced, and the product washed with H_2O, NaOH aq., and H_2O, and dried in a desiccator. Yield, 13 g. (92%); f. p. 17·85°, m. p. 17·98°, showing the absence of by-products. Cryst. twice from $Pr^{\alpha}OH$–MeOH and 3 times from acetone, it had const. f. p. 18·10°, m. p. 18·13°, identical with the values for cetane from spermaceti (Part II; J., 1932, 740).

Propionic acid can be used instead of AcOH, and would be the better solvent for iodides of high mol. wt.

A solution of cetyl bromide (14·5 g.) in AcOH (250 c.c.) was boiled for 10 hr. with frequent additions of Zn dust. The product contained Br, 7·8% (Calc. for $C_{16}H_{33}Br$: Br, 26%).

Cetyl chloride was mostly unchanged after 20 hr.

Octadecane.—A boiling solution of pure octadecyl iodide (5·7 g.) (m. p. 32·94°) in AcOH (150 c.c.) was reduced with Zn for 4·5 hr., and the product washed free from iodide and dried for 2 days in a desiccator. Yield, 3·7 g. (97%) of octadecane, f. p. 27·5°, m. p. 27·7°. Cryst. from pure acetone, it had f. p. 27·5°, m. p. 27·6° (transparent form), m. p. 28·02° (opaque form), unchanged by crystn. from acetone and then from C_6H_6–acetone. These values are higher (0·2°, 0·1°) than those for the octadecane (Part II; *loc. cit.*) from hydrogenation of octadecene–cetene mixtures. As the iodide was undoubtedly pure, the new values are preferred.

In the older specimen it was difficult to observe the metastable form, unless cetane was added. When the new specimen is cooled without stirring, it crystallises in transparent branching clusters at 27·5° and these seem to melt at 27·6°, but also change to the opaque form, m. p. 28·02°. After most of the solid has melted, the temp. begins to rise and the opaque suspension of fine crystals does not clear when kept for 20 min. at 29° (stirring). At 29·7° it clears sharply. As this can be repeated indefinitely, the clearing-point being 29·7° ± 0·1°, after short or long standing, it appears that a third form of octadecane has been detected.

Method (*ii*). *Reduction with Zinc–Copper Couple.*—Zn dust was washed with 5% H_2SO_4, and H_2O, and covered with $CuSO_4$ aq. (2%), which was replaced when almost decolorised. The metal was washed with H_2O and then EtOH.

A mixture of cetyl iodide (9 g.), EtOH (50 c.c. of 95%), and Zn–Cu (25 g.) was refluxed for 8 hr., cooled, and filtered. Ice-water pptd. from the filtrate 5 g. (yield, 90%) of solid free from I. Cryst. from PrOH–MeOH, it melted at 18°.

Method (*iii*). *Catalytic Reduction.*—The Pd–$CaCO_3$ catalyst used by Harington (*Biochem. J.*, 1926, **20**, 304) for the reduction of thyroxine in KOH aq. had to be activated for use in Pr$^{\alpha}$OH. $CaCO_3$ (50 g., freshly prepared) was stirred in H_2O (400 c.c. at 80°), $PdCl_2$ (0·5 g. in 20 c.c. H_2O) added, and then CH_2O (2 c.c. formalin in 20 c.c. H_2O). After 2 mins.' stirring, the dark solid was filtered off, washed with warm H_2O, EtOH, and PrOH, and used immediately.

To a solution of cetyl iodide (8 g.) in PrOH (30 c.c.), KOH (3 g. in 20 c.c. PrOH) and the catalyst (25 g.) were added. After shaking with H for 2 hr. at 20°, the theo. vol. (515 c.c.) had been absorbed and reaction ceased. The solution was removed from the catalyst (washing with hot PrOH), and ice-water pptd. cetane, m. p. 17—18°, free from I (yield, 90%).

Cetyl Formate.—This was prepared from pure cetyl alcohol and HCO_2H and crystallised from ligroin. It was dimorphous : transparent form, f. p. 22·7°, and opaque form, m. p. 25°, (in capillary tube, 26°) (Found : C, 75·4; H, 12·7. Calc. for $C_{17}H_{34}O_2$: C, 75·5; H, 12·6%) (cf. Rheinbolt, König, and Otten, *Annalen*, 1929, **473**, 249).

According to D.R.-P. 296741 (Friedländer's " Fortschritte," 1915, **13**, 929) the formate on distillation in vac. should lose CO_2 and yield a paraffin. It could be distilled unchanged at 200°/20 mm., and even at 310°/760 mm. CO_2 could only just be detected. Addition of Fe or charcoal was without effect. When refluxed for 2·5 hr. and then distilled, the ester had m. p. 21—22·5° and was easily sol. in MeOH, in which cetane is sparingly sol. The examples mentioned in the patent allow a temp. of 290° with a pressure of 10—15 mm. to be maintained and this may account for the difference. No evidence, however, of identification of the products is given.

An application to cetyl iodide of the Rosenmund method of reducing acid chlorides in xylene solution with H_2–Pd–$BaSO_4$ (*Ber.*, 1918, **51**, 594) was unsuccessful. Some HI was evolved, but most of the halide was unchanged.

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