

NOTES

1-Methyl-2-n-propylphenanthrene. By G. A. R. KON, E. S. NARRACOTT, and C. REID.

1-Methyl-2-n-propylphenanthrene, which was required for comparison with a hydrocarbon isolated in the course of another research, has been prepared by a standard method. Ethyl *n*-propylmalonate was condensed with β -1-naphthylethyl bromide, the product hydrolysed and decarboxylated to γ -1-naphthyl- α -*n*-propylbutyric acid, the chloride of which was cyclised to 1-keto-2-n-propyl-1 : 2 : 3 : 4-tetrahydrophenanthrene; this with methylmagnesium iodide gave a carbinol, which underwent dehydration to the dihydro-derivative of the required hydrocarbon; the final dehydrogenation was carried out with palladised charcoal.

100 G. of ethyl *n*-propylmalonate were added to 18.5 g. of "molecular" potassium in 250 c.c. of benzene; the mixture was warmed for $\frac{1}{2}$ hour, then boiled for 48 hours with 75 g. of β -1-naphthylethyl bromide. The product was isolated by addition of water and distillation of the benzene solution. The fraction (33 g.), b. p. 203—211°/2.5 mm., was boiled with 25 g. of potassium hydroxide in 30 c.c. of water and enough alcohol to effect solution; 22 g. of β -1-naphthylethyl-*n*-propylmalonic acid were ultimately obtained as an oil, which soon solidified and had m. p. 173° (decomp.) after crystallisation from benzene-petroleum (Found: C, 71.9; H, 6.5. $C_{18}H_{20}O_4$ requires C, 72.0; H, 6.7%).

Attempts to decarboxylate the acid by boiling with water (compare Fieser and Seligman, *J. Amer. Chem. Soc.*, 1935, 57, 2174) failed and 35 g. of it were therefore heated above its m. p., and the product distilled under 2 mm. pressure, the yield of γ -1-naphthyl- α -*n*-propylbutyric acid being 25 g. This gradually solidified and crystallised from dilute alcohol in small rhombs, m. p. 68—69° (Found: C, 79.4; H, 8.0. $C_{17}H_{20}O_2$ requires C, 79.6; H, 7.9%).

25 G. of the preceding acid were left overnight with 10 c.c. of thionyl chloride in 200 c.c. of petroleum, the solution warmed for $1\frac{1}{2}$ hours, and the solvent distilled under reduced pressure. The residue was taken up in 200 c.c. of carbon disulphide and treated with 10 g. of finely powdered aluminium chloride in small portions. After 12 hours, dilute hydrochloric acid was added, and 1-keto-2-n-propyl-1 : 2 : 3 : 4-tetrahydrophenanthrene isolated in the usual way (19 g.), b. p. 206—208°/5 mm.; it solidified at once and separated from dilute alcohol (charcoal) in lustrous plates, m. p. 53° (Found: C, 85.7; H, 7.8. $C_{17}H_{18}O$ requires C, 85.7; H, 7.6%); it formed a semicarbazone, m. p. 210—202°.

19 G. of the ketone in 100 c.c. of ether were dropped into a solution of the Grignard reagent prepared from 5.8 c.c. of methyl iodide, and the mixture then boiled for an hour. The product was isolated in the usual way, treated with semicarbazide acetate to remove any unchanged ketone (none was found), and distilled under reduced pressure, some water then being eliminated. 1-Methyl-2-n-propyl-3 : 4-dihydrophenanthrene was finally distilled over sodium, b. p. 208—210°/13 mm.; in another preparation it was purified by percolation of a petroleum solution through a column of activated alumina, but it did not solidify (Found: C, 92.0; H, 8.2. $C_{18}H_{20}$ requires C, 91.5; H, 8.5%).

8 G. of the dihydro-compound were heated under reflux with 4 g. of 10% palladised charcoal for 4 hours at 250—300°. The product was then thoroughly extracted with petroleum (b. p. 40—60°), and the solution allowed to percolate through a 30 cm. column of activated alumina. On evaporation, 6 g. of 1-methyl-2-n-propylphenanthrene were recovered, which formed plates, m. p. 54°, from methyl alcohol (Found: C, 92.2, 92.3; H, 7.6, 7.5. $C_{18}H_{18}$ requires C, 92.3; H, 7.7%). The orange picrate had m. p. 97° (Found: C, 62.1; H, 4.4. $C_{18}H_{18}, C_6H_3O_7N_3$ requires C, 62.2; H, 4.6%); the yellow *s*-trinitrobenzene complex formed needles, m. p. 112°, from methyl alcohol (Found: C, 64.9; H, 4.7. $C_{18}H_{18}, C_6H_3O_6N_3$ requires C, 64.4; H, 4.7%), the trinitrotoluene complex, pale yellow needles, m. p. 82—83°, from methyl alcohol (Found: C, 65.3; H, 5.0. $C_{18}H_{18}, C_7H_5O_6N_3$ requires C, 65.0; H, 5.0%), and the styphnate, dark yellow needles, m. p. 118—119°, from methyl alcohol (Found: C, 60.1; H, 4.2. $C_{18}H_{18}, C_6H_3O_8N_3$ requires C, 60.1; H, 4.4%).

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An Improved Method for the Preparation of α -Chlorocrotonic Acid. By JOHN C. ROBERTS.

THE method for the preparation of α -chlorocrotonic acid given in Beilstein's "Organische Chemie," involving reaction between butylchloral hydrate and potassium ferrocyanide (Wallach, *Ber.*, 1877, 10, 1530), is troublesome and gives poor yields when fairly large quantities of the acid are required. The following method (compare Krämer and Pinner, *Annalen*, 1871, 158, 50) gives superior results.

Butylchloral hydrate (50 g.), when added to 100 c.c. of nitric acid (d , 1.504), dissolves easily and the solution becomes cold. This is kept at 30—35° for 1½ hours with intermittent shaking and at the ordinary temperature for 24 hours; the acid is then distilled until the temperature of the vapour is 135°. The residue, on cooling, forms colourless crystals of trichlorobutyric acid (47 g.). This is mixed with 200 c.c. of water (it does not dissolve completely and a lower oily layer forms), and zinc dust (30 g.) slowly added; a vigorous reaction occurs. The mixture is heated on a water-bath for 3 hours and cooled, concentrated hydrochloric acid (30 c.c.) added, and the α -chlorocrotonic acid extracted with ether (70 + 50 + 40 c.c.). The combined extracts are washed with water and dried (sodium sulphate), the solvent evaporated, and the product dried over concentrated sulphuric acid in a desiccator. The α -chlorocrotonic acid (26 g.) has m. p. 99—100° (Wislicenus, *Annalen*, 1888, 248, 293, gives 99.2°). Yield, 83.5% of the theoretical, calculated on the butylchloral hydrate. The ethyl ester has b. p. 174—176° (corr.) [Perkin, J., 1894, 65, 424, gives 175—176° (corr.)].

The method is superior to that of Wallach in that (i) the evolution of large quantities of hydrogen cyanide is avoided and (ii) the yield of α -chlorocrotonic acid is nearly doubled (Wallach's method gives 44.3% of the theoretical yield).—UNIVERSITY COLLEGE, NOTTINGHAM.
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