

CCX.—*The Purification of Some Sensitive Ketones.*

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IN the course of experiments, which are still in progress, on the action of acid catalysts on *cyclohexylideneacetone* the observation was made that cold dilute sulphuric acid had but little isomerising action on the ketone. This suggested a possible method for the regeneration of *cyclohexylideneacetone* and related compounds from their semicarbazones, a process usually involving very extensive isomerisation. Thus, for instance, *isopulegonesemicarbazone* gives up to 60% of pulegone on hydrolysis with oxalic acid in a current of steam (Hugh and Kon, J., 1927, 2585).

isoPulegonesemicarbazone appeared particularly suitable for an investigation of the problem. It was soon found that oxalic acid in ether, even in the cold and in theoretical quantity, produced appreciable conversion of *isopulegone* into pulegone, but better results were obtained by using very dilute sulphuric acid and replacing the ether by a large volume of an indifferent solvent to remove the ketone formed from the sphere of reaction.

The method adopted in practice consists in mechanically shaking the semicarbazone, suspended in light petroleum (b. p. 40—60°), with the calculated amount of *N*/2-sulphuric acid until hydrolysis is complete and no more solid remains; there is, however, no danger in continuing the shaking, as the aqueous layer no longer contains free acid. The amount of sulphuric acid required to effect hydrolysis of a semicarbazone is theoretically 98 g. for one gram-molecule, because semicarbazide forms an acid sulphate; in practice, however, half that amount can be used when dealing with a very sensitive ketone and the acid can with advantage be diluted with two or three volumes of water.

Even *isopulegone*, which is the most mobile substance studied in these laboratories, can be obtained in a state of purity by the process described. Its properties, together with those of several other ketones, now obtained pure for the first time, are recorded in the experimental portion.

The properties of *cyclopentylideneacetone* differ appreciably from those given by Dickens, Hugh, and Kon (J., 1929, 572), notably the exaltation of the molecular refraction and the iodine value; the latter suggests that the value for the equilibrium of the ketone with its $\beta\gamma$ -form and for the corresponding ethyl ketone given there is too near the $\alpha\beta$ -side; the correct figure is probably nearer 77% $\alpha\beta$. The same remark applies also to *cycloheptylideneacetone*, because the ketone used by Hugh, Kon, and Mitchell (J., 1929, 1435) for their reference curve had an iodine addition of about 30%; the proper equilibrium value in this case is probably about 60% $\alpha\beta$.

EXPERIMENTAL.

isoPulegone.—In the first experiments, the pure semicarbazone and crystallised oxalic acid, in quantity sufficient to produce the ketone and semicarbazide hydrogen oxalate, were shaken in ethereal suspension. After 3 days, the solid was filtered off and the ketone formed was recovered. It had n_D 1.47113 and an iodine addition of 56% in 10 minutes by the method of Linstead and May (J., 1927, 2565); it therefore contained some 35% of *pulegone*.

A satisfactory result was obtained when the semicarbazone (4.2 g.) was mechanically shaken with 250 c.c. of light petroleum (b. p. 40—60°) and 35.6 c.c. of 0.562*N*-sulphuric acid for 2 days. The ketone recovered had an iodine addition of 65.4%, which equals the best value previously obtained. The semicarbazone prepared from it melted in the crude state at about 150°, and at 174—175° after one crystallisation. Reducing the amount of petroleum leads to a less pure product: in subsequent experiments the amount was increased to 300 c.c. for each batch of 4.18 g. (2/100 g.-mol.) and

100 c.c. of water were added to dilute the $N/2$ -acid and a product of perfectly reproducible properties was invariably obtained. This boiled at $100.5^\circ/18$ mm. and had $d_4^{21.0^\circ}$ 0.91785 and n_D 1.46718, whence $[R_L]_D = 45.99$; its iodine addition was 66.0%. These properties are regarded as characteristic of pure *isopulegone* and differ somewhat from the values quoted by Hugh and Kon (*loc. cit.*).

The above method of regeneration was applied to the ether-soluble portion of *isopulegonesemicarbazone*; this was recrystallised first from acetone and then from methyl alcohol and melted (not sharply) at 169° . The ketone obtained from it evidently contained some *pulegone* which must have been present in the original crude ketone (iodine addition, 62.1%).

Other Ketones.—When working with less sensitive ketones it is advisable to use sufficient $N/2$ -acid to form the acid sulphate of semicarbazide (80 c.c. for 2/100 g.-mol.).

The following ketones have now been prepared in the pure state by the process described :

Δ^1 -*cyclo*Hexenylacetone, b. p. $80^\circ/15$ mm., $d_4^{28.4^\circ}$ 0.93901, $n_D^{18.4^\circ}$ 1.47300, $[R_L]_D$ 41.26, iodine addition 84.9% in 10 minutes.

*cyclo*Hexylideneacetone, b. p. $83^\circ/9$ mm., $d_4^{29.5^\circ}$ 0.94586, $n_D^{19.5^\circ}$ 1.49223, $[R_L]_D$ 42.38, iodine addition 13.4% in 10 minutes.

Δ^1 -*cyclo*Hexenylmethyl ethyl ketone, b. p. $92^\circ/10$ mm., $d_4^{33^\circ}$ 0.93022, $n_D^{19.3^\circ}$ 1.47291, $[R_L]_D$ 45.87, iodine addition 89.5% in 10 minutes.

*cyclo*Hexylidenemethyl ethyl ketone. The hydrolysis of the high-melting form of the semicarbazone required more than 3 days. The ketone had b. p. $110^\circ/20$ mm., $d_4^{18.2^\circ}$ 0.93622, $n_D^{18.2^\circ}$ 1.49118, $[R_L]_D$ 47.08, and an iodine addition of 10.7% in 10 minutes; another specimen, prepared from the lower-melting semicarbazone, had an addition of about 10% and practically identical physical properties.

*cyclo*Pentylideneacetone, b. p. $74-76^\circ/14$ mm., $d_4^{20.5^\circ}$ 0.94282, $n_D^{20.5^\circ}$ 1.48541, $[R_L]_D$ 37.75, iodine addition 14.9% in 5 minutes and 17.9% in 10 minutes.

Pulegone, b. p. $109^\circ/19$ mm., $d_4^{16.9^\circ}$ 0.93808, $n_D^{16.9^\circ}$ 1.48810, $[R_L]_D$ 46.73, iodine addition 10.6% in 10 minutes.

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