easily by means of their optical properties: the propyl crystallizing from 95% alcohol in acicular crystals with parallel extinction, the butyl and amyl both forming rhombic plates with symmetrical extinction and easily distinguished from each other by their different optic axial angles (36°40′ *versus* 20°30′).

The ethyl and the isoamyl derivatives both melt at 101–102°, but they differ in appearance, the ethyl derivative crystallizing in elongated plates with parallel extinction, while the isoamyl derivative crystallizes in rhombs with symmetrical extinction. Similarly, the *o*- and *p*-tolyl derivatives melting within 2° of each other differ greatly in the magnitude of the optic axial angle, and while both form acicular crystals, the former crystallizes in fine needles, the latter in short rods.

Summary

The optical properties of a number of phenylthiourea derivatives have been determined and have been shown to be useful in distinguishing between members of a homologous series, particularly when these have very nearly identical melting points.

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NOTES

A Method for Preparing *ortho*-Deuterium

BY L. FARKAS AND L. SANDLER

In the following an apparatus is described by which ortho-deuterium of comparatively high concentration can be prepared without the use of liquid hydrogen. The low temperature necessary for the para–ortho conversion of deuterium is reached by adiabatic desorption of hydrogen from charcoal pre-cooled by solid air. This method was developed by Simon[1] and already has been used for other purposes.

The apparatus is shown in Fig. 1. It consists of three main parts. The upper part with the ground joint A leads to an oil pump (Megavac) and contains the inner charcoal vessel (N) in which the deuterium is adsorbed and converted. This part may also be used for the preparation of para-hydrogen by means of solid air, if a Dewar vessel, fitting into the joint (A), is used and the liquid air is pumped off through tap 1. The second part is the outer charcoal vessel (Y) which essentially is a Dewar vessel containing about 180 cc. of charcoal. The space (S) between the walls of (Y) can either be evacuated or filled with hydrogen through three-way tap no. 3. Surrounded by the charcoal, in the middle of the vessel (Y), a test-tube (T) is fitted loosely on (N). This arrangement ensures that the outer vessel can be detached rapidly from the upper part, when the deuterium is to be desorbed. The third part of the apparatus serves for pre-cooling the outer charcoal vessel by means of solid air and consists of a metal case containing a Dewar vessel filled with liquid air. It must be chosen large as a considerable loss of liquid air takes place while pumping off its vapor and adsorbing hydrogen. The metal lid is detachable and is made vacuum tight with Apiezon sealing compound.

Experimental Procedure.—First the charcoal in (N) is heated *in vacuo* for some time to 150–200°. Then (Y) containing test-tube and charcoal is attached to the high vacuum system by the joints (A) and (B) and the charcoal in it is outgassed. At this stage the space (S) is filled with hydrogen. Subsequently the vessel (Y) is immersed in liquid air, the metal container is closed and the liquid air pumped off. (Y) should be clamped directly above the lid in order to prevent it from being sucked into the metal case. During the time the liquid air is pumped off, (N) is connected with the deuterium reservoir and the charcoal in (Y) is saturated with dry hydrogen under atmospheric pressure. The process of adsorption in both vessels is allowed to go on for a few hours until it eventually comes to a standstill, indicating that the lowest possible temperature is reached by the pumping process. Approximately 60 °K. is attained in this way and the orthodeuterium concentration in (N) is about 75%. Taps 2 and 4 are now closed and the thermal contact between the solid air and (Y_0) is interrupted by evacuating (S) through tap 3. The hydrogen absorbed on the charcoal in (Y) is then pumped off through tap 1. The temperature fall during

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(1) F. Simon, *Physik. Z.*, **27**, 790 (1926), and *Physica*, IV, **9**, 879 (1937); *cf.* further references there.

this procedure is followed by measuring the deuterium pressure above the inner charcoal. For example, in the course of one hour the deuterium pressure sank from an initial value of 6 mm. (at 60°K.) to 0.013 mm. When the pressure is slowly rising again the process is interrupted. The metal case and the outer vessel are detached quickly by admitting air into (S) and (Y) through taps 2 and 3. The deuterium is rapidly desorbed by blowing air at (N) and is collected in a reservoir. From 5 cc. of charcoal saturated with deuterium under 0.013 mm. pressure, about 300 cc. of gas (at S. T. P.) was desorbed. The desorption of the gas was practically completed in ten seconds. Its ortho-concentration was about 82%, corresponding to a temperature of 45°K.

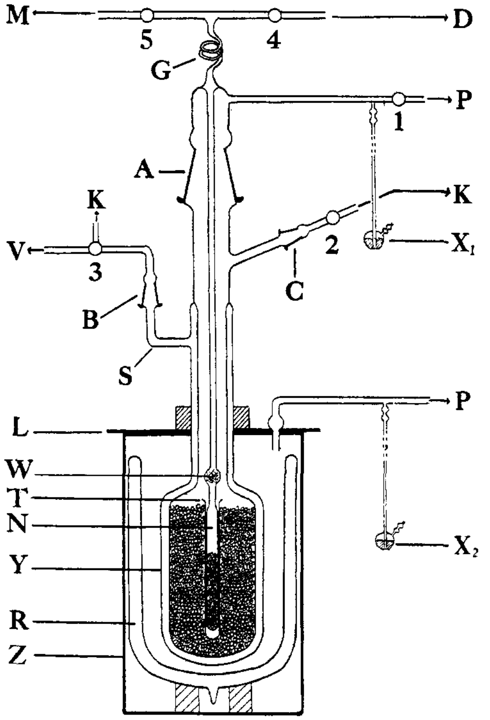

Fig. 1.—M, to high vacuum and McLeod gage; D, to deuterium reservoirs; G, glass spiral; P, to oil pump; K, to Kipp generator for hydrogen; V, to high vacuum; X_1, excess pressure valve 1; X_2, excess pressure valve 2; L, lid; W, glass wool; T, test-tube; N, inner charcoal vessel; Y, outer charcoal vessel; R, dewar flask; Z, metal case; 1, 2, 3, 4, 5, taps.

The equilibrium concentrations of p-H_2 and o-D_2 at different temperatures are listed in Table I.

TABLE I

Temp., °K.	Concn., % p-H_2	Concn., % o-D_2	Excess concn., % p-H_2	Excess concn., % o-D_2	Method by which obtainable
200	25.0	66.7	0.0	0.0	High temp. equil.
85	45.4	69.1	20.4	2.4	Liq. air
60	65.4	74.8	40.4	*8.1*	Solid air
45	82.9	82.1	57.9	*15.4*	Desorption
20	99.8	98.0	74.8	31.3	Liq. H_2

By using ortho-deuterium prepared by the desorption method, the concentration range available is nearly doubled and thus the accuracy of measurement of a conversion rate is much improved. This has been made use of lately in investigations concerning the paramagnetic conversion of hydrogen.[2]

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[2] L. Farkas and L. Sandler, *J. Chem. Phys.*, **8**, 248 (1940).

An Effect of Carbonyl Derivatives as Impurities in Alcohols

BY B. J. FONTANA AND T. D. STEWART

In studying the equilibrium

$$(CH_3)_2C(OH)CN \overset{K_I}{\rightleftarrows} (CH_3)_2C{=}O + HCN$$

in various alcohols as solvents, the data were examined by plotting c against b/c, where b is the initial concentration of the cyanohydrin and c the equilibrium value of hydrocyanic acid and acetone. The usual equilibrium expression can be put in the form

$$c = K_I b/c - K_I$$

In the cases, methanol, ethanol, butanol, 2-methylpropanol and t-butyl alcohol, the plot gave straight lines with intercept of unity on the b/c axis; in propanol, 2-propanol, 2-butanol and pentanol the lines were straight (perhaps fortuitously) but the intercept greater than unity. The alcohols were purified in general by distillation through a three-meter (about 18-plate) column, with and without lime present. In some cases they were dehy-

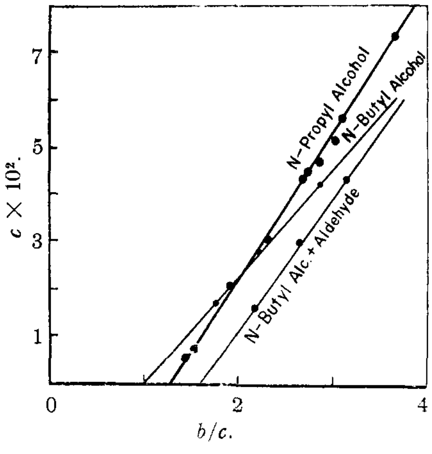

Fig. 1.—The effect of aldehyde impurity upon the dissociation of acetone cyanohydrin in propanol and butanol.