tered on a Gooch crucible, washed with a mixture of 25 ml. of 2 *N* hydrochloric acid and 25 ml. of ethyl alcohol, then with 75 ml. of 2 *N* hydrochloric acid. The precipitate was then washed with water until free of chlorides, and dried in an oven at 95° until it reached a constant weight.

The purest sample of dodecanal (0.1431 g.) gave 0.2744 g. of the hydrazone, or 97.2% of the amount which should be obtained if the aldehyde were pure and was quantitatively converted to the hydrazone which was isolated and purified without loss.

The aldehydes and ketones were characterized by the following derivatives: *n*-butyraldehyde, b. p. 70–75° (740 mm.), 2,4-dinitrophenylhydrazone, m. p. 121–122°; *i*-butyraldehyde, b. p. 63–68° (740), gave isobutylidene malonic ester; trimethylacetaldehyde, b. p. 74–76° (739); 2,4-diphenylhydrazone, m. p. 210–211°, semicarbazone, m. p. 191–192°; *n*-hexanal, b. p. 126–129° (740), 2,4-dinitrophenylhydrazone, m. p. 106°, semicarbazone, m. p. 112–113°; 2-ethylhexanal, b. p. 161–166° (737), 2,4-dinitrophenylhydrazone, m. p. 122–123°; *n*-dodecanal, b. p. 138–139° (22), 2,4-dinitrophenylhydrazone, m. p. 107–108°, semicarbazone, m. p. 102–103°; heptanone-2, b. p. 147–148° (747), m. p. semicarbazone, 122–123°; heptanone-4, b. p. 142–145°.

Summary

A practical and useful method has been described whereby the alcohols of four or more carbon atoms per molecule may be dehydrogenated to aldehydes or ketones in the liquid phase. The reaction is carried out under a pressure of ethylene, which serves as an acceptor for the hydrogen split out of the alcohol under the influence of a suitable catalyst, such as copper chromite or preferably a mixed catalyst containing copper, zinc, nickel and barium chromites.

MADISON, WISCONSIN RECEIVED AUGUST 19, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Optical Properties of Phenylthiourea Derivatives[1]

BY MARY L. WILLARD AND MARGARET Z. JONES

Phenylthiourea derivatives are useful for the characterization of primary and secondary amines.[2] To enhance this usefulness, and particularly to make it possible to distinguish more readily between members of homologous series, the optical properties of these substances have now been studied.

The symmetrical derivatives were prepared from aromatic amines and carbon bisulfide; the unsymmetrical from phenyl isothiocyanate and various amines. Their melting points, which are in reasonable agreement with the values recorded in the literature, and the observed optical properties are collected in the table.

TABLE I

DERIVATIVES OF PHENYLTHIOUREA

Derivative	M. p., °C.	Habit	Ext.	Opt. ax. angle 2 *V* Obsd.	Opt. ax. angle 2 *V* Calcd.	Refractive index α	Refractive index β	Refractive index γ
N-Methyl-N′-	112–113	Tab.	Par.		88	1.662	1.695	1.730
N-Ethyl-N′-	101–102	Tab.	Par.		82	1.650	1.680	1.720
N-*n*-Propyl-N′-	64	Aci.	Par.	$56^1/_3$	56	1.690	1.700	1.735
N-*n*-Butyl-N′-	63	Tab.	Sym.	$36^2/_3$		1.590	1.603	1.775 (est.)
N-*n*-Amyl-N′-	68–69	Tab.	Sym.	$20^1/_2$		1.620	1.630	1.76 (est.)
N-*i*-Amyl-N′-	101–102	Tab.	Sym.	Large[c]		1.620	1.700	
N-β-Hydroxyethyl-N′-	138	Aci.	Par.	..[c]		1.675	1.692	
N,N′-Di-[a]	154	Tab.	Sym.	82		1.645	1.720	High
N-*o*-Tolyl-N′-	138	Aci.	Par.	$35^1/_3$	36	1.655	1.663	1.74 (est.)
N-*p*-Tolyl-N′-	139–140	Aci.	Par.	63		1.610	1.675	1.8 (est.)
N,N′-Di-*o*-tolylthiourea	158	Aci.	Par.	$66^2/_3$	$64^1/_2$	1.655	1.663	1.725
N,N′-Di-*p*-tolylthiourea[b]	178	Aci.	Par.[d]	$42^1/_2$	46	1.675	1.685	1.74 (est.)
N-*o*-Chlorophenyl-N′-	158	Aci.	Par.	$29^1/_3$			1.72	

[a] Arzruni (*Ber.*, **19**, 1821 (1886)) reports this substance to form rhombic crystals of short prismatic habit, with positive double refraction and apparent axial angle in sodium light, 2H in bitter-almond oil, of $95^2/_3$°. [b] Levin (*Z. Krist.*, **7**, 519 (1883)) reports this substance as rhombic. [c] Sign negative (doubtful). [d] Sometimes oblique.

As can be seen from the table the normal propyl, butyl and amyl derivatives, all of which melt within a range of 6°, can be distinguished

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[1] Presented before the Division of Microchemistry at the 99th meeting of the American Chemical Society, Cincinnati, Ohio.

[2] The preparation and properties of the primary aromatic amine derivatives have been given by Otterbacher and Whitmore (THIS JOURNAL, **51**, 1909 (1929)).

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.

STATE COLLEGE, PENNSYLVANIA RECEIVED JUNE 24, 1940

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.