

**delta-d-bornylsemicarbazide and delta-d-neobornylsemicarbazide / by J.A. Goodson.**

### **Contributors**

Goodson, John Augustus.  
Wellcome Chemical Research Laboratories.

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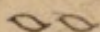
Wellcome Collection  
183 Euston Road  
London NW1 2BE UK  
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$\delta$ -*d*-BORNYLSEMICARBAZIDE AND  
 $\delta$ -*d*-*neo*BORNYLSEMICARBAZIDE

BY

J. A. GOODSON

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THE WELLCOME CHEMICAL RESEARCH LABORATORIES  
(The Wellcome Foundation Ltd.)

T. A. HENRY, D.Sc., *Director*

6, King Street, Snow Hill

LONDON, E.C. 1







## CCLXII.— $\delta$ -d-Bornylsemicarbazide and $\delta$ -d-neoBornylsemicarbazide.

By JOHN AUGUSTUS GOODSON.

FOR an investigation, which has so far given negative results, the author has had occasion to prepare a quantity of  $\delta$ -d-bornylsemicarbazide and  $\delta$ -d-neobornylsemicarbazide. The use of such optically active semicarbazides for the resolution of racemic carbonyl compounds has been suggested by various workers and a number of them have been prepared, *e.g.*, camphoryl- $\psi$ -semicarbazide (Forster and Fierz, J., 1905, **87**, 722),  $\delta$ - $\alpha$ -phenylethylsemicarbazide (Wilson, Hopper, and Crawford, J., 1922, **121**, 866), and  $\delta$ -menthylsemicarbazide (Wilson and Crawford, J., 1925, **127**, 103), whilst Forster and Attwell attempted to prepare  $\beta$ -bornylsemicarbazide (J., 1904, **85**, 1188), but in no case have these substances so far been used successfully for this purpose.  $\delta$ -d-Bornylsemicarbazide



and  $\delta$ -*d*-neobornylsemicarbazide were only tried on one racemic ketone, viz., 3-methylcyclohexanone, and although well-crystallised products were obtained, they did not separate into optical antipodes on fractional crystallisation from two solvents.

### EXPERIMENTAL.

*Acetone- $\delta$ -d-bornylsemicarbazone*.—To *d*-bornylamine (10 g.) melted by immersion in an oil-bath at  $175^\circ$ , was added acetone-semicarbazone (7.5 g.) a little at a time, and the heating continued for 15 minutes. The cold crystalline product was recrystallised from alcohol, and active *acetone- $\delta$ -d-bornylsemicarbazone* obtained in anhydrous needles (yield, 76%), m. p.  $141\text{--}148^\circ$  (corr.),  $[\alpha]_D^{20} + 25.5^\circ$  ( $c = 2.04$  in dry alcohol) (Found: C, 66.7; H, 10.0; N, 16.5.  $C_{14}H_{25}ON_3$  requires C, 66.9; H, 10.0; N, 16.7%).

In order to obtain a good yield, it is necessary to use anhydrous *d*-bornylamine. In a preliminary experiment, *d*-bornylamine containing two molecules of water of crystallisation, obtained by precipitation with sodium hydroxide from a solution of the hydrochloride, was used; a considerable quantity of di-*d*-bornylcarbamide was then produced.

*$\delta$ -d-Bornylsemicarbazide Hydrochloride*.—Acetone- $\delta$ -*d*-bornylsemicarbazone (85 g.) and 10% hydrochloric acid (850 c.c.) were heated on the water-bath for  $1\frac{1}{2}$  hours.  *$\delta$ -Bornylsemicarbazide hydrochloride* crystallised on cooling and was recrystallised from alcohol after removal of a small quantity of di-*d*-bornylcarbamide by filtration (yield, 94%). The anhydrous substance, m. p.  $190\text{--}198^\circ$  (corr.), had  $[\alpha]_D^{20} + 2.6^\circ$  ( $c = 5$  in dry alcohol) (Found in air-dried substance: loss at  $105^\circ$  in a vacuum, 14.1.  $C_{11}H_{22}ON_3Cl \cdot 2H_2O$  requires  $H_2O$ , 12.7%. Found in anhydrous substance: C, 53.1; H, 8.9; Cl, 14.2.  $C_{11}H_{22}ON_3Cl$  requires C, 53.3; H, 9.0; Cl, 14.3%).

*$\delta$ -d-Bornylsemicarbazide*.— *$\delta$ -d-Bornylsemicarbazide hydrochloride* (10 g.) dissolved in a little alcohol was treated with 8.5 c.c. of 20% sodium hydroxide solution and poured into water. The base was extracted with chloroform and obtained in needles by addition of light petroleum to the concentrated solution. The substance, dried in a vacuum at  $50^\circ$ , melted at  $75^\circ$  after softening some degrees lower, and had  $[\alpha]_D^{20} + 17.0^\circ$  ( $c = 5$  in dry alcohol). On keeping, it gradually decomposed (Found in dried substance: C, 62.5; H, 10.4.  $C_{11}H_{21}ON_3$  requires C, 62.5; H, 10.0%).

*$\delta$ -d-Bornylsemicarbazones* of various ketones were prepared by adding the requisite quantity of ketone to a concentrated solution of the base in alcohol.

*isoPulegone- $\delta$ -d-bornylsemicarbazone*, prepared from *isopulegone*



having  $\alpha_D^{18} - 6.0^\circ$ , crystallised in thick, rhombic plates, m. p.  $224-226^\circ$  (corr.),  $[\alpha]_D^{20} + 9.2^\circ$  ( $c = 5.04$  in chloroform) (Found: C, 72.8; H, 10.1.  $C_{21}H_{35}ON_3$  requires C, 73.0; H, 10.2%).

4-Methylcyclohexanone- $\delta$ -*d*-bornylsemicarbazone crystallised in clusters of six-sided plates, softening slightly at  $145^\circ$  (corr.), melting at  $154^\circ$  (corr.), and having  $[\alpha]_D^{20} + 27.2^\circ$  ( $c = 4.898$  in dry alcohol) (Found: C, 70.5; H, 10.2.  $C_{18}H_{31}ON_3$  requires C, 70.8; H, 10.2%).

3-Methylcyclohexanone- $\delta$ -*d*-bornylsemicarbazone, prepared from optically inactive 3-methylcyclohexanone, melted at  $172-177^\circ$  (corr.) and had  $[\alpha]_D^{20} + 27.4^\circ$  ( $c = 4.85$  in dry alcohol) (Found: C, 70.5; H, 10.1.  $C_{18}H_{31}ON_3$  requires C, 70.8; H, 10.2%). Recrystallisation from alcohol or ligroin failed to resolve it into its components, even when seeded with *d*-3-methylcyclohexanone- $\delta$ -*d*-bornylsemicarbazone, m. p.  $173-179^\circ$  (corr.),  $[\alpha]_D^{20} + 7.4^\circ$  ( $c = 4.726$  in dry alcohol) (Found: C, 70.4; H, 10.1.  $C_{18}H_{31}ON_3$  requires C, 70.8; H, 10.2%), prepared from *d*-3-methylcyclohexanone kindly supplied by Dr. Kenyon.

Acetone- $\delta$ -*d*-neobornylsemicarbazone, prepared in the same way as acetone- $\delta$ -*d*-bornylsemicarbazone, but at  $190^\circ$  in order to keep the neobornylamine liquid, crystallised from alcohol in anhydrous needles, m. p.  $175-179^\circ$  (corr.),  $[\alpha]_D^{20} - 92.1^\circ$  ( $c = 2.008$  in dry alcohol) (Found: C, 66.6; H, 10.1.  $C_{14}H_{25}ON_3$  requires C, 66.9; H, 10.0%).

$\delta$ -*d*-neobornylsemicarbazide hydrochloride was prepared by hydrolysis of the above acetone derivative with dilute hydrochloric acid. The anhydrous substance melted at  $198-202^\circ$  (corr.) and had  $[\alpha]_D^{20} - 50.8^\circ$  ( $c = 4.982$  in dry alcohol) (Found in air-dried substance: loss at  $105^\circ$  in a vacuum, 5.3.  $C_{11}H_{22}ON_3Cl \cdot H_2O$  requires  $H_2O$ , 6.8%. Found in substance dried at  $105^\circ$  in a vacuum: Cl, 14.1.  $C_{11}H_{22}ON_3Cl$  requires Cl, 14.3%).

$\delta$ -*d*-neobornylsemicarbazones were prepared by adding the requisite quantity of ketone to a concentrated solution of  $\delta$ -*d*-neobornylsemicarbazide in alcohol.

4-Methylcyclohexanone- $\delta$ -*d*-neobornylsemicarbazone crystallised in rosettes of needles, m. p.  $151-155^\circ$  (corr.),  $[\alpha]_D^{20} - 91.3^\circ$  ( $c = 2.83$  in dry alcohol) (Found: C, 70.4; H, 10.0.  $C_{18}H_{31}ON_3$  requires C, 70.8; H, 10.2%).

3-Methylcyclohexanone- $\delta$ -*d*-neobornylsemicarbazone, prepared from optically inactive 3-methylcyclohexanone, melted at  $157-161^\circ$  (corr.) and had  $[\alpha]_D^{20} - 91.2^\circ$  ( $c = 4.772$  in dry alcohol) (Found: C, 70.6; H, 10.3.  $C_{18}H_{31}ON_3$  requires C, 70.8; H, 10.2). Recrystallisation from alcohol or ligroin failed to resolve it into its components.



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