CCLXII.—δ-d-*Bornylsemicarbazide and* δ-d-neo*Bornylsemicarbazide.*

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FOR an investigation, which has so far given negative results, the author has had occasion to prepare a quantity of δ-*d*-bornylsemicarbazide and δ-*d*-*neo*bornylsemicarbazide. 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-ψ-semicarbazide (Forster and Fierz, J., 1905, **87**, 722), δ-α-phenylethylsemicarbazide (Wilson, Hopper, and Crawford, J., 1922, **121**, 866), and δ-menthylsemicarbazide (Wilson and Crawford, J., 1925, **127**, 103), whilst Forster and Attwell attempted to prepare β-bornylsemicarbazide (J., 1904, **85**, 1188), but in no case have these substances so far been used successfully for this purpose. δ-*d*-Bornylsemicarbazide and δ-*d*-*neo*bornylsemicarbazide were only tried on one racemic ketone, *viz.*, 3-methyl*cyclo*hexanone, and although well-crystallised products were obtained, they did not separate into optical antipodes on fractional crystallisation from two solvents.

EXPERIMENTAL.

Acetone-δ-d-*bornylsemicarbazone*.—To *d*-bornylamine (10 g.) melted by immersion in an oil-bath at 175°, 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*-δ-d-*bornylsemicarbazone* obtained in anhydrous needles (yield, 76%), m. p. 141—148° (corr.), $[\alpha]_D^{20^\circ}$ + 25·5° (*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.

δ-d-*Bornylsemicarbazide Hydrochloride*.—Acetone-δ-*d*-bornylsemicarbazone (85 g.) and 10% hydrochloric acid (850 c.c.) were heated on the water-bath for 1½ hours. δ-*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—198° (corr.), had $[\alpha]_D^{20}$ + 2·6° (*c* = 5 in dry alcohol) (Found in air-dried substance: loss at 105° in a vacuum, 14·1. $C_{11}H_{22}ON_3Cl,2H_2O$ 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%).

δ-d-*Bornylsemicarbazide*.—δ-*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°, melted at 75° after softening some degrees lower, and had $[\alpha]_D^{20^\circ}$ + 17·0° (*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%).

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

iso*Pulegone*-δ-d-*bornylsemicarbazone*, prepared from *iso*pulegone having $\alpha_D^{18°}$ − 6·0°, crystallised in thick, rhombic plates, m. p. 224—226° (corr.), $[\alpha]_D^{20°}$ + 9·2° (*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-*Methyl*cyclo*hexanone*-δ-d-*bornylsemicarbazone* crystallised in clusters of six-sided plates, softening slightly at 145° (corr.), melting at 154° (corr.), and having $[\alpha]_D^{20°}$ + 27·2° (*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-*Methyl*cyclo*hexanone*-δ-d-*bornylsemicarbazone*, prepared from optically inactive 3-methyl*cyclo*hexanone, melted at 172—177° (corr.) and had $[\alpha]_D^{20°}$ + 27·4° (*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-*methyl*cyclo*hexanone*-δ-d-*bornylsemicarbazone*, m. p. 173—179° (corr.), $[\alpha]_D^{20°}$ + 7·4° (*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-methyl*cyclo*hexanone kindly supplied by Dr. Kenyon.

Acetone-δ-d-neo*bornylsemicarbazone*, prepared in the same way as acetone-δ-*d*-bornylsemicarbazone, but at 190° in order to keep the *neo*bornylamine liquid, crystallised from alcohol in anhydrous needles, m. p. 175—179° (corr.), $[\alpha]_D^{20°}$ − 92·1° (*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%).

δ-d-neo*Bornylsemicarbazide hydrochloride* was prepared by hydrolysis of the above acetone derivative with dilute hydrochloric acid. The anhydrous substance melted at 198—202° (corr.) and had $[\alpha]_D^{20°}$ − 50·8° (*c* = 4·982 in dry alcohol) (Found in air-dried substance: loss at 105° in a vacuum, 5·3. $C_{11}H_{22}ON_3Cl,H_2O$ requires H_2O, 6·8%. Found in substance dried at 105° in a vacuum: Cl, 14·1. $C_{11}H_{22}ON_3Cl$ requires Cl, 14·3%).

δ-*d*-*neo*Bornylsemicarbazones were prepared by adding the requisite quantity of ketone to a concentrated solution of δ-*d*-*neo*bornylsemicarbazide in alcohol.

4-*Methyl*cyclo*hexanone*-δ-d-neo*bornylsemicarbazone* crystallised in rosettes of needles, m. p. 151—155° (corr.), $[\alpha]_D^{20°}$ − 91·3° (*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-*Methyl*cyclo*hexanone*-δ-d-neo*bornylsemicarbazone*, prepared from optically inactive 3-methyl*cyclo*hexanone, melted at 157—161° (corr.) and had $[\alpha]_D^{20°}$ − 91·2° (*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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