

THE ISOMERIC 4-*n*-PROPYLCYCLOHEXANOLS

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*Received December 6, 1948*

In a previous communication from this laboratory (1) it was shown that mixtures of isomers resulting from the reduction of 4-*n*-propylcyclohexanone with platinum in acetic acid gave viscosities much smaller ( $\eta^{25}$  0.098–0.125 than either of the pure isomers ( $\eta^{25}$  0.313 and 0.688) or a mixture of approximately equal amounts of the isomers ( $\eta^{25}$  0.456). Since the molecular refractions of the low-viscosity mixtures agreed closely with the calculated value, it was tentatively suggested that the mixtures might contain a third stable isomer. Further investigations of solid 4-substituted cyclohexanols have shown that *cis* and *trans* forms of such compounds exist in only one form and no other isomers are present since all mixtures can be explained on the basis of the melting point-composition diagrams of the pure isomers (2). A subsequent reinvestigation of the low-viscosity mixtures of the 4-*n*-propylcyclohexanols has established the presence of a small amount of 4-*n*-propylcyclohexanone.

The ketone was separated by fractional distillation of the mixture (66.0 g.) through a 30-plate Fenske column under reduced pressure with a reflux ratio of approximately 50:1. It boiled at 97–98° (20 mm.), yield 5.3 g., and had  $d_{25}^{25}$  0.9002,  $n_D^{25}$  1.4530,  $\eta^{25}$  0.0278. The semicarbazone melted at 181–182° and did not depress the melting point of an authentic specimen. The low viscosity of the contaminating ketone ( $\eta^{25}$  0.0227 for purified 4-*n*-propylcyclohexanone) explains the abnormal values obtained for the viscosities of the mixtures.

Unchanged ketone remains in mixtures of isomeric alkylcyclohexanols obtained by catalytic hydrogenation over platinum catalyst even though the theoretical amount of hydrogen is taken up because of the accompanying hydrogenolysis of the hydroxyl group.

Similar abnormally low viscosities ( $\eta^{25}$  1.55) have been observed by v. Auwers and Dersch some time ago for the cyclohexanol mixture obtained by reduction by 2-methylcyclohexanone with platinum in acetic acid (3). Derivatives of the *trans* alcohol could be isolated from mixtures with viscosities corresponding to that of the pure *cis* isomer ( $\eta^{25}$  1.71). The postulated inversion of the *cis* alcohol suggested by the authors as a possible explanation for these results has been disproven independently by Skita and Faust (4) and by Hückel and Hagenguth (5). It is now reasonable to assume that v. Auwers' mixtures contained 2-methylcyclohexanone ( $\eta^{20}$  0.0176) (6).

## REFERENCES

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