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Short Communications

Pinacols from *o*-Aminoacetophenone

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Recently the electrolytic reduction of *o*-aminoacetophenone was reported;[1] among the products were 1-(2′-aminophenyl)ethanol, two stereoisomers of 3-acetyl-4-amino-7-hydroxy-7-methyl-2,6-methano-2,5,6,7-tetrahydro-1(1H)benzazonine, and the two pinacols VI (m.p. 183°) and VII (m.p. 134–136°). It was, however, not proved which of the pinacols was the D,L- or the *meso*-form, respectively.

It has now been found that pinacol VI (m.p. 183°) can be resolved in a D- and an L-form and pinacol VII (m.p. 134–136°) is thus the *meso*-form. Pinacol VI was resolved by means of D-camphoric acid which precipitated predominantly the D-form. After recrystallization of the precipitate it was decomposed with alkali and the D-pinacol isolated. From the mother liquor the L-pinacol was obtained.

The assignment of pinacol VI as the D,L-mixture is in accordance with the result obtained from the NMR-spectrum; according to considerations of the most favoured conformation of acetophenone pinacols, based on hydrogen bond formation, the D,L-pinacol has its methyl signal at higher and hydroxyl signal at lower field compared to the *meso*-pinacol.[2] The presence of the amino groups thus does not invalidate the rule in this case.

The D,L/*meso*-ratio for the pinacols from *o*-aminoacetophenone is dependent on pH (pH 1.5, D,L/*meso* 1.14; pH 13, D,L/*meso* 2.5) in the same manner as the pinacols from acetophenone,[2] but different from the ratio obtained from 2-acetopyridine[3] (1.5 M acetic acid, D,L/*meso* 0.75; 2 M potassium acetate, D,L/*meso* 0.3). The basic centre in 2-aminoacetophenone does thus not play the same role in determining the product as that in 2-acetopyridine.

Experimental. Resolution of pinacol VI. Pinacol VI (0.4 g) and D-camphoric acid (0.6 g) were dissolved in 3 ml dioxane and allowed to cool. After some time a precipitate A (0.79 g) was formed which was recrystallized from dioxane. The composition of the precipitate (0.26 g) corresponded to 1 mole pinacol, 2 moles camphoric acid, and 2 moles dioxane (Found: C 62.90; H 8.11; N 3.31. Calc. for $C_{44}H_{68}N_2O_4$: C 62.27; H 8.02; N 3.30). Titration of the pinacol salt with base was in accordance with this formulation.

The pinacol salt (0.88 g) was refluxed with a mixture of 2 N potassium hydroxide (10 ml) and ethanol (10 ml) for 4 h. After cooling, the precipitate (0.2 g) was filtered off and recrystallized from ethanol; the D-pinacol VI (0.13 g) had m.p. 205–207°, $[\alpha]_D^{23.5} = +152° \pm 5°$ (ethanol). (Found: C 70.58; H 7.15; N 10.39. Calc. for $C_{16}H_{20}N_2O_2$: C 70.56; H 7.40; N 10.39). The IR-spectrum (KBr) of the D-pinacol was not significantly different from that of the D,L-pinacol.

The mother liquor from precipitate A was evaporated to dryness *in vacuo* and the residue treated with alkali as described above. The mixture was extracted with chloroform which was then dried (potassium carbonate) and evaporated. After recrystallization the L-pinacol had m.p. 202°, $[\alpha]_D^{23.5} = -157° \pm 5°$ (ethanol).

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2. Stocker, J. H. and Jenevein, R. M. *J. Org. Chem.* 33 (1968) 294, 412, 2145.
3. Stocker, J. H. and Jenevein, R. M. *Symposium on "The Synthetic and Mechanistic Aspects of Electroorganic Chemistry"*, Durham, N.C., USA, October 1968; Abstract, p. 221.

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