CHEMISTRY

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reaction scheme

Figure 1: reaction scheme

isomerization scheme

Figure 2: isomerization scheme

Abstract

Full Text

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THE ACTION OF FORMAMIDE ON ISOMERIC METHYLENEDICYCLOHEXANONE AND TRICYCLOHEXANOLONE

(Presented by Academician B. A. Kazanskii, December 23, 1957)

Acting on the recently described methylenedicyclohexanone (I) (^{1,2}) and its isomer, tricyclohexanolone (II) (^{1}), with formamide under the conditions of the Leuckart reaction, in both cases we obtained the same compounds, namely: sym-octahydroacridine (III) and perhydroacridine (IV):

This fact indicates that, under the reaction conditions, II isomerizes into I:

and the process proceeds at a sufficient rate (otherwise the principal reaction products would be the products of hydroamination of II).

The reaction established is also of interest from a preparative standpoint: it proceeds quite smoothly and with a good yield (~80%) of bases, and is readily accessible both with respect to the technique of carrying it out and in terms of the starting materials. This favorably distinguishes it from the previously known methods for obtaining these bases ($^{3-5}$).

Finally, it should be noted that this is the first example of the application of the Leuckart reaction to alicyclic 1,5-diketones. Previously the Leuckart reaction had been carried out on several examples of 1,5-diketones of the aliphatic and arylaliphatic series (^{6,7}).

Experimental Part

Experiments with diketone [I] and ketol (II) were conducted under completely identical conditions. A solution of one of the indicated compounds (1 mole) in formamide* (12 moles) was heated in a flask with a reflux air condenser at 155-170° (thermometer in the mixture) until the evolution of CO_2 ceased (~4 hr). The hot solution was then poured into a 5-6-fold volume of ~10% aqueous sodium hydroxide solution and boiled on a wire gauze for about 2 hr. After cooling, the separated oil was extracted with benzene or ether.

* Formamide was prepared according to (8).

The extract was dried over calcined magnesium sulfate. After removal of the solvent, the residue was distilled in vacuo:

52% distilled at 98-105°/2.5 mm (1st fraction)
14% distilled at 113-116°/0.5 mm (2nd fraction)
33.5% remained in the distillation flask; this residue rapidly crystallized.

sym-Octahydroacridine ($C_{13}H_{17}N$). The crystallized residue, after pressing on a clay plate and recrystallization from petroleum ether, has a constant m.p. 69.5°. Literature data: 69° (3,4); 73.5-74° (5); 71° (9); 68-70° (1). A mixed-melting-point test with an authentic sample of sym-octahydroacridine, prepared by method (1), gives no depression.

Found, %: N 7.75; M 189.
$C_{13}H_{17}N$. Calculated, %: N 7.50; M 187.

Picrate—m.p. 197.5-199° (from alcohol); a mixed-melting-point test with the picrate of an authentic sample gives no depression.

Perhydroacridine ($C_{13}H_{23}N$). The distillate (both fractions) crystallizes already during distillation. After pressing on a clay plate and recrystallization from petroleum ether, the crystals—in the form of white needles—have a constant m.p. 87-88.5°. Literature data for perhydroacridine: 80° (3), 91° (5).

Found, %: C 80.60; 80.57; H 11.90; 12.10; N 7.18; 7.26; M 192; 189
$C_{13}H_{23}N$. Calculated, %: C 80.82; H 11.91; N 7.25; M 193

Picrate—yellow needle-like crystals, m.p. 179-181° (from alcohol).

Acetylperhydroacridine is formed when a mixture of 0.7 g of the base with 1 ml of acetic anhydride is evaporated on a boiling water bath in vacuo. The residue (0.45 g) crystallizes. Colorless four- and six-sided plates (from alcohol), when heated in a capillary, decompose without melting in the range 150-160°.

Found, %: CH_3CO 17.73
$C_{13}H_{22}NCOCH_3$. Calculated, %: CH_3CO 18.30

Perhydroacridine hydrochloride is readily formed by the action of concentrated hydrochloric acid on the base. White needle-like crystals (from alcohol) are sparingly soluble in water and in cold alcohol, and insoluble in benzene. When heated in a capillary they decompose at 220-230°, without melting.

Found, %: Cl 15.30
$C_{13}H_{23}NHCl$. Calculated, %: Cl 15.47

Reduction of octahydroacridine to perhydroacridine. The octahydroacridine obtained is very smoothly reduced by sodium and absolute alcohol in the presence of catalytic amounts (∼ 3% of the base taken) of nickel formate to perhydroacridine. The perhydroacridine obtained in this way was identical (mixed-melting-point test) with that described above.

In the absence of nickel formate, we were unable to obtain good results with respect to the yield of perhydroacridine.

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Note: Figure translations are in progress. See original paper for figures.