

EFFECT OF TITANIUM COMPOUNDS ON THE REDUCTION
OF OXIMES OF THE 4-CHROMANONE TYPE

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We have established that the addition of TiCl_4 (as well as FeCl_3) to LiAlH_4 (LAH) suppresses rearrangement during the reduction of oximes, in contrast to the known effect of AlCl_3 , which substantially increases the yields of rearrangement products.

The addition of TiCl_4 (or FeCl_3) to LAH in the reduction of 4-chromanone and 4-thiochromanone oximes leads to the formation of only 4-aminochroman (I) and 4-aminothiochroman (II), respectively (in 68 and 74% yields). Only primary amines - α -phenethylamine (III) and benzhydrylamine (IV), respectively (in 67 and 78% yields) - were also obtained as a result of reduction by the same method of acetophenone and benzophenone oximes, which were taken for comparison.

One mole of the oxime per 3 moles of LAH and the metal chloride were used. The amines were isolated in the form of the hydrochlorides, the identification of which and analysis of which for the possible presence of secondary amines were accomplished by thin-layer chromatography (on Al_2O_3), gas-liquid chromatography (GLC) (with monitoring by means of introduction into the starting reaction mixture of 7 mole % of the authentic secondary amine; the sensitivity of the determination was $\leq 3\%$), and PMR spectroscopy with the use of genuine samples of the primary and secondary amines. In addition to primary amines I-IV, secondary amines in 50, 43, 18, and 50% yields, respectively, with respect to the overall yields of the amines are formed when the reduction of the indicated oximes with LAH was carried out under the same conditions without the addition of TiCl_4 or FeCl_3 .

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