ASYMMETRIC HYDROGENATION OF OXIME OF DIETHYL ESTER OF α-KETOGLUTARIC ACID

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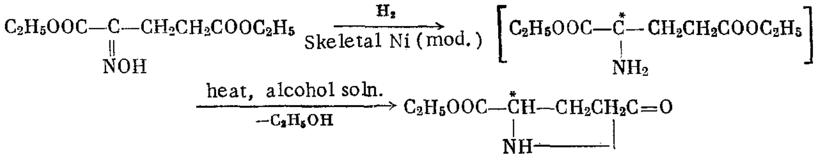
UDC 541.63:542.941:547.485

The oxime of the diethyl ester of α-ketoglutaric acid undergoes asymmetric hydrogenation in nonpolar solvents on a skeletal Ni catalyst that had been treated with optically active amino acids; the isolated L-glutamic acid had $[\alpha]_D + 0.4\text{-}0.6°$ [1]. We ran the reduction of the oxime of the diethyl ester of α-ketoglutaric acid on the same catalyst in ethanol solution. From the reaction products we isolated only the ethyl ester of pyroglutamic acid in 12% yield, bp 143-145° (1.5 mm); $[\alpha]-1.6°$ (in aqueous solution). Found: C 53.15; H 6.7; N 8.5%. $C_7H_{11}O_3N$. Calculated: C 53.3; H 7.00; N 8.9%. Srong absorption bands at 1690, 1700, 1735 and 3250-3340 cm^{-1} are observed in the IR spectrum of the reaction product.

The formation of the ethyl ester of pyroglutamic acid can be accomplished via the cyclization of the reduction product, namely the diethyl ester of L-glutamic acid, which occurs when the latter is heated in alcohol medium [2].



$$C_2H_5OOC{-}\underset{\underset{NOH}{\|}}{C}{-}CH_2CH_2COOC_2H_5 \xrightarrow[\text{Skeletal Ni (mod.)}]{H_2} \left[C_2H_5OOC{-}\underset{\underset{NH_2}{|}}{\overset{*}{C}}{-}CH_2CH_2COOC_2H_5\right] \xrightarrow[-C_2H_5OH]{\text{heat, alcohol soln.}} C_2H_5OOC{-}\underset{\underset{NH}{|}}{\overset{*}{C}H}{-}CH_2CH_2C{=}O$$

LITERATURE CITED

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2. C. Okinaka, Sexagint. Festschrift fur Y. Ocaka, Kyoto (1927), p. 30; Chem. Zbl., 9, 2399 (1928).

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2819-2820, December, 1972. Original article submitted July 3, 1972.