Note on the Preparation of Ethyl Cyclohexylidene-Cyanoacetate

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Ethyl cyclohexylidene-cyanoacetate has been prepared by the condensation of ethyl cyanoacetate and cyclohexanone under pressure[1] and in the presence of various catalysts i. e. sodium ethoxide[2], piperidine[2],[3],[4],[5], pyridine[6], piperazine[6], acid amides, soluble salts of amines or quarternary ammonium bases with an organic acid[7], acetamide[8],[6] and ammonium acetate and acetic acid[9]. Best yields (89%) were obtained with acetamide and continuous separation of water formed during the reaction[8]. In modifying the procedure reported for the preparation of the methyl ester[10] i.e. using the diethylamine as a catalyst at room temperature and without separating the water formed during the reaction, yields higher than previously mentioned[8] were obtained.

EXPERIMENTAL

The mixture of ethyl cyanoacetate (1130 g, 10 moles), cyclohexanone (2940 g, 30 moles) and diethylamine (51,1 g, 0,7 mole) was stirred for eight hours at room temperature. Benzene (1100 ml) was added and the separated water removed. The benzene solution was washed with diluted sulfuric acid and water, dried over anhydrous sodium sulfate and the solvent evaporated. After removing the excess of cyclohexanone and the unreacted ethyl cyanoacetate under reduced pressure, 1755 g (90,8%) of ethyl cyclohexylidene-cyanoacetate were obtained, b. p. 120—125°/1,5 mm (112—114°/1,5 mm[11] 125°/4 mm[12] D^{20} : 1,055 (D_4^{18} : 1,0556[4], D^{25} : 1,052[8]),

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n_D^{19} : 1,5053 ($n_D^{19,5}$: 1,4967[13]). Refractionation of fore-runnings increased the yield to 1824 g (94,3%).

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IZVOD

Bilješka o pripremi etil cikloheksiliden-cianoacetata

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Modifikacijom postupka za pripremu metil cikloheksiliden-cianoacetata[10]) dobiveni su optimalni uslovi za pripremu etilnog estera kondenzacijom etil cianoacetata i cikloheksanona uz dietilamin kao katalizator. Postupak je jednostavan (sobna temperatura, bez istovremenog odjeljivanja reakcijom nastale vode) i daje dobra iskorištenja (94,3%).

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