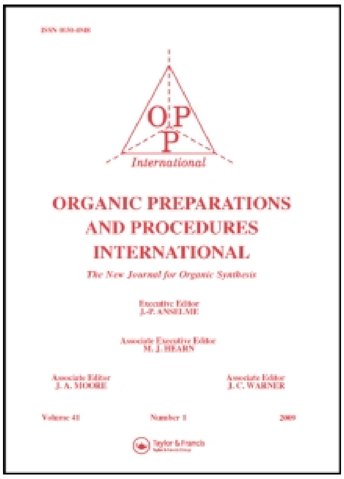
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A SIMPLIFIED SYNTHESIS OF *CIS*-PENT-2-EN-4-YN-1-OL

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A SIMPLIFIED SYNTHESIS OF CIS-PENT-2-EN-4-YN-1-OL

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The synthesis of trans-pent-2-en-4-yn-1-ol by the reaction of two equivalents of sodium acetylide with epichlorohydrin was first reported in 1947;[1] a later study[2] indicated that cis-pent-2-en-4-yn-1-ol was formed in less than 0.1% in this reaction. The latter authors expressed the opinion that since the absence of the cis isomer could not be readily explained mechanistically, the cis isomer was formed but was lost via further reactions (e.g. cyclization). They subsequently synthesized cis-pent-2-en-4-yn-1-ol from acrolein in a 1.5% overall yield.

Landor and Pepper[3] extended the reaction of epichlorohydrin with alkali metal acetylides to form trans-alk-2-en-4-yn-1-ols and furans and were also unable to isolate any of the "valuable cis-pent-2-en-4-yn-1-ol."

We have found that substitution of lithium acetylide for sodium acetylide in the reported procedure[1] affords a 1:1 mixture of cis and trans-pent-2-en-4-yn-1-ol in 47% yield. The pure cis-pent-2-en-4-yn-1-ol was isolated in 15% yield by careful fractional distillation. The lesser tendency of the lithium salt of cis-pent-2-en-4-yn-1-ol to undergo cyclization to 2-methylfuran is probably due to its more covalent character as compared to the sodium salt.

EXPERIMENTAL[4]

Pent-2-en-4-yn-1-ol.- To a solution of lithium acetylide in liquid ammonia (1.5 l) [prepared from 22.9 g (3.30 moles) of lithium using the ferric nitrate catalyst[5] to catalyze the formation of lithium amide] epichlorohydrin (158.6 g, 1.72 moles) was added under nitrogen with stirring over a 2 hr period. When the addition of epichlorohydrin was complete, the mixture was stirred for 5 hrs and then solid ammonium chloride (188.6 g, 3.52 moles) was slowly added. The ammonia was allowed to evaporate and 800 ml of ether was added. The solid residue obtained on filtration was dissolved in water and the solution was filtered to remove a small quantity of tar and then thoroughly extracted with ether. The combined ethereal solution was washed with cold 10% sulfuric acid, water, and then dried over sodium sulfate. The solvent was removed under vacuum and the residual oil fractionated on a 24" teflon spinning band column to give 21.55 g (15%) of cis-pent-2-en-4-yn-1-ol, bp. 83-86°/56 mm, $n_D^{21.5}$ 1.4882, p-phenylazobenzoate, mp. 81-82°, lit.[2] bp. 68-69°/19 mm, $n_D^{21.5}$ 1.4882, p-phenylazobenzoate, mp. 83.5-84.5°. The last fraction consisted of 24.98 g (17%) of slightly impure trans-pent-2-en-4-yn-1-ol, bp. 96-98°/56 mm, n_D^{23} 1.4913, p-phenylazobenzoate, mp. 103-104°, lit.[6] bp. 90°/50 mm, n_D^{23} 1.4933, p-phenylazobenzoate, mp.[2] 102-103°. Middle fractions were obtained (19.62 g, 14%), bp. 87-93°/56 mm, n_D^{23} 1.4903-1.4907 which were mixtures of the cis and trans isomers as shown by vapor phase chromatography (6 ft. column packed with 5% Apiezon L on Chromosorp P; flow rate - 60 ml/min; temperature - 80°C).

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