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Short Communication

PREPARATION OF I-BROMO-4-METHYLPENT-3-ENE

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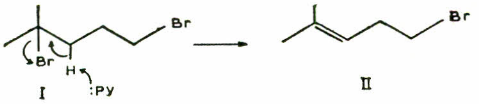
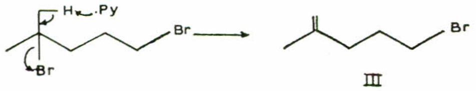
William and Schinz[1] reported the preparation of 1-bromo-4-methylpent-3-ene (II) by the action of pyridine on 2-methylpentan-2,5-dibromide (I) through the following mechanism.



The IR spectrum of the bromide (II) shows a strong band at ν_{max} (film) 895 cm^{-1} which proves the presence of a terminal methylene group ($C{=}CH_2$). The NMR spectrum of the product shows a multiplet at δ 4.73 which is characteristic for a terminal methylene group. However, the product is not resolved by GLC (10% P.E.G.A./Celite at 75°).

It is, therefore, concluded that the pyridine can also attack the hydrogen atom of the methyl group to give an isomeric bromide (III) with a terminal methylene group as under:



The quantitative measurements through NMR spectrum show the product to be a mixture of 80% bromide (II) and 20% bromide (III). However, the pure bromide (II) is obtained using the method of Medina and Manjarrez.[3]

Experimental

The IR spectrum was recorded on a Unicam SP 200 spectrometer with a polystyrene film calibration. NMR spectrum was recorded on a Varian A-60 spectrometer in deuterochloroform using TMS as an internal reference.

Preparation of 1-Bromo-4-methylpent-3-ene. A mixture of 2-methylpentan-2, 5-dibromide (32 g) and dry pyridine (11.1 g) was stirred under reflux at 90° for 45 min. The solution was kept at 100–105° for 15 min when a white solid, pyridine hydrobromide separated. The crude product was transferred to a distillation flask with anhydrous ether. Distillation gave a colourless liquid (16 g, 75%) b.p. 57–58°/17 mm, n_D20 1.4453 (lit.[114] b.p. 84–85°/84 mm; n_D16 1.4458). ν_{max} (film) 840 ($C{=}C{-}H$), 896 ($C{=}CH_2$, terminal methylene), 1390, 1455 (CH_2, CH_3), 1645, 1655 ($C{=}C$) cm^{-1} δ 1.65 (s, $CH_3{-}C{=}C$), 1.7 (bs, (CH,$-C{=}C$), 2.53 (bq, $CH{-}CH_2{-}CH_2Br$, J 7Hz), 3.33 (m, $CH_2{-}Br$), 4.73 (m, $C{=}CH_2$, terminal methylene), 5.12 (t, $CH{=}C$, J 7Hz, fine splitting J 1Hz and 1.5 Hz). The NMR measurements indicated the product to be a mixture of 1-bromo-4-methylpent-3-ene and 1-bromo-4-methylpent-4-ene in an approximate ratio of 80:20% respectively GLC (10% P.E.G.A./Celite at 75°) could not resolve two isomeric bromides.

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References

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3. F. Medina and A. Manjarrez, Tetrahedron, **20,** 1807 (1964).