Isocyclic Compounds

1987

Bridged Compounds

Q 0060

8707-160

Norbornan-2-ols and Brendan-2-ols in the Ritter Reaction. — The Ritter reaction according to method A) of exo- or endo-norbornan-2-ol (I), 1-methylnorbornan-exo-2-ol (III), exo-brendan-2-ol (VII) and endo-brendan-2-ol (XI) affords the corresponding acetylamines (II), (IV)—(VI), and (VIII)—(X). Reduction of the acetyl compounds (VIII)—(X) yields the secondary amines (XIIa)—(XIVa) and alkaline hydrolysis of (VIII)—(X) gives the primary amines (XIIb)—(XIVb). The formations of the acetylamines occur via carbocations. The compounds (V), (VI), (IX) and (X), in particular, result from Wagner—Meerwein rearrangements of the intermediary carbocations. — (GEVORKYAN, G. G.; ORDUBADI, M. D.; BELIKO-VA, N. A.; PEKHK, T. I.; Zh. Org. Khim. 22 (1986) 9, 1885—92; Moskovskii gos. univ. im. Lomonosova; Russ.) — Schönefeld

d R' RT - CN

1987

Isocyclic Compounds

XII XIII

NH-R

XIV NH-R

a R:-Et

b R:-H

Bridged Compounds

Q 0060 8707-161 Tricyclo|5.1.0.0^{2.8}|oct-3-ene, -oct-4-ene, and -octane: Preparation and Thermolysis of the Hydro Derivatives of Octavalene. — Debromination of the tetrabromobicyclo-octene (I) with LiAlH₄ leads, via allylic rearrangement, to the tribromide (II), treatment of which with Bu — Li affords the monobromide (III). Further debromination gives the tricyclooctene (IV), and hydrogenation of (IV) using diimine (generated from triisopropylbenzenesulfonic hydrazide according to the method of Reese) results in the formation of the tricyclooctane (V) with the bicyclooctene (VI) as byproduct. The isomer (X) of (V) is prepared from (I) via the rearranged nitrate (VII). — Compounds (IV) and (V) rearrange on heating almost quantitatively to give (XI) and a (XIII)/(XIV) mixture, resp., whereas (X) is thermally decomposed to yield a complex mixture of products, of which only (XII) is identified. — A new route to octavalene (XVI) is elaborated by treatment of its 4-bromo derivative (XV) with tert-butyl lithium with no formation of a mentionable quantity of cyclooctatetraene as side product. — (CHRISTL*, M.; HERZOG, C.; KEMMER, P.; Chem. Ber. 119 (1986) 10, 3045—58; Inst. Org. Chem., Univ. Würzburg, D-8700 Würzburg; Ger.) — Betcke