1988 Isocyclic Compounds

Bridged Compounds

0 0060

8851-144

Synthesis and Ritter Reaction of 2,5,5,6-Tetramethylbicyclo[2.2.1]heptane-2-endo-ol. — The reaction between the camphor analogue (I) and methyllithium (II) affords the title compound (III). The Ritter reaction with acetonitrile (IV) gives an inseparable 2:1 mixture of the isomeric amides (V) and (VI). Their formation probably proceeds via non-classical carbocations, which undergo Wagner—Meerwein rearrangements. The structures of (V) and (VI) are further confirmed by spectral characterization of the corresponding amines, which are prepared by LiAlH4 reduction. — (KOZLOV, N. G.; POPOVA, L. A.; VALIMAE, T. K.; KNIZHNIKOV, V. A.; OL'DEKOP, YU. A.; Zh. Org. Khim. 24 (1988) 7, 1452—1456; Inst. fiz.-org. khim. Akad. nauk Belorusskoi SSR, Minsk; Russ.) — Schönefeld

Me MeLi (II) Me MeCN (IV), conc.
$$H_2SO_4$$
 $V + VI$

Me Me OH OH

III 89%

Bridged Compounds

Q 0060

8851-145

Reaction of cis-Bicyclol4.3.0|nona-3,7-diene with Iodine. Synthesis of Tricyclol4.3.0.0^{3,7}|nona-4,8-diene (Brexa-4,8-diene). — The iodination of the bicyclo[4.3.0]nonadiene (I) proceeds via transannular cyclization to afford a mixture of eight isomeric iodides in 70% overall yield. Among these the diodo derivative (II) is the only product that can be isolated pure. It is characterized by ¹H and ¹³C NMR and by mass spectra. On treatment of (II) with tBuOK, exo-cis-elimination of HI occurs to give the endo-9-iodobrexene (III). This compound, on treatment with tBuOK at 120 °C eliminates HI to give the hitherto unknown brexa-4,8-diene (IV) which is also obtained from the diiodide (II). The mechanism of the transannular

Isocyclic Compounds

1988

cyclization, which occurs on iodination of (I), is discussed. — (LUKOVSKAYA, E. V.; BOBYLEVA, A. A.; PEHK, T. I.; DUBITSKAYA, N. F.; PETRUSHENKO-VA, I. A.; BELIKOVA, N. A.; Zh. Org. Khim. 24 (1988) 7, 1457—1463; Moskovskii gos univ. im. Lomonosova; Russ.) — Schönefeld

Bridged Compounds

Q 0060

8851-146

Synthesis of Homoiceane (V) (Tetracyclo[6.3.1.1^{2.7}.0^{4.10}|tridecane) and 3,13-Dehydrohomoiceane (VI) (Pentacyclo[7.3.1.0^{2.4}.0^{3.8}.0^{5,11}|tridecane) Through Homo-Diels—Alder Reaction (no yields given for the mixture (V)/(VI)). — (YAMAGUCHI*, R.; BAN, M.; KAWANISI, M.; Bull. Chem. Soc. Jpn. 61 (1988) 8, 2909—2912; Dep. Ind. Chem., Fac. Eng., Kyoto Univ., Yoshida, Kyoto 606; Eng.) — Lehmann

