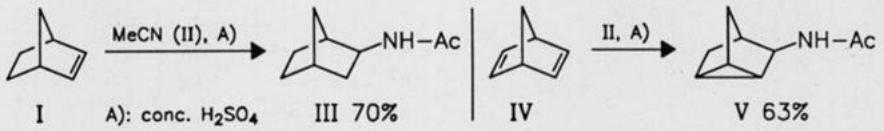
Bridged Compounds

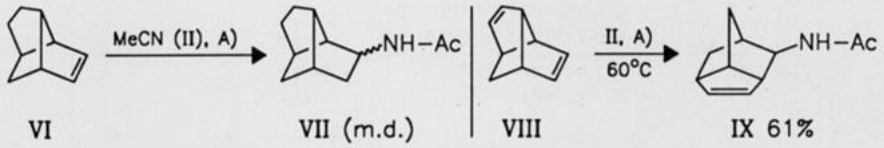
Q 0060

8950-133

Unsaturated Hydrocarbons of the Norbornane and Brexane Series in the Ritter Reaction. — Under the conditions of the Ritter reaction, norbornene (I) affords the expected exo-configurated 2-acetyl derivative (III), whereas norbornadiene (IV) undergoes rearrangement of the cation intermediate to yield the tricyclene (V). The mechanism of its formation is not quite clear. Brex-4-ene (VI) affords a mixture of products, whose main components are the exo and endo isomers (VII), which are formed via protonation at C-4 of the starting (VI). Brexa-3,8-diene (VIII) is protonated exclusively at C-5 to yield the product (IX) after rearrangement of the cation intermediate. The methods described here establish a convenient access to the derivatives (III), (V) and (IX). Finally, the reactivities of the four starting compounds are compared. The reactivity follows this sequence: (IV) < (I) < (VI) ≈ (VIII). — (BOBYLEVA, A. A.; PETRUSHCHENKOVA, I. A.; LUKOVSKAYA, E. V.; PEKHK, T. I.; DUBITSKAYA, N. F.; BELIKOVA, N. A.; Zh. Org. Khim. 25 (1989) 7, 1428—1436; Moskovskii gos. univ. im. Lomonosova; Russ.) — Schönefeld



I A): conc. H_2SO_4 III 70% IV V 63%



VI VII (m.d.) VIII IX 61%

m.d.: mixture of diastereomers

Bridged Compounds

Q 0060

8950-134

Rearrangement Approach to Bridgehead Substitution of 1-Methoxybicyclo[2.2.2]oct-5-en-2-ones. — A formal bridgehead-substitution of the methoxybicyclo[2.2.2]octenones (I), derived stereoselectively from anisoles by the Diels—Alder strategy followed by Birch reduction and isomerization, leads to the products (V), which are of interest as potential precursors of [5-5] fused ring systems such as (VIII) via triplet-sensitized photochemical oxa-di-π-methane rearrangement. The diquinane (VIII) is a known precursor of (±)-gymnomitrol (IX). — (UYEHARA*, T.; OSANAI, K.; SUGIMOTO, M.; SUZUKI, I.; YAMAMOTO, Y.; J. Am. Chem. Soc. 111 (1989) 18, 7264—7265; Dep. Chem., Fac. Sci., Tohoku Univ., Sendai 980, Jap.; Eng.) — Kieslich