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CYCLOBUTYL-CYCLOPROPYLCARBINYL REARRANGEMENT OF 4,4-DICHLOROTETRACYCLO[3.3.0.0^{2,8}.0^{3,6}]OCTANES

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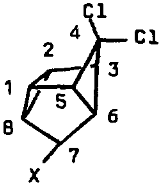
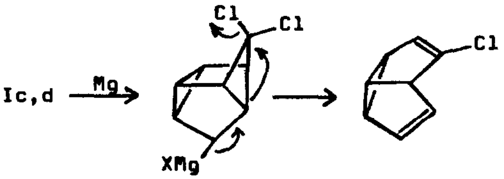
Due to the presence of a cyclopropylcarbinyl as well as a cyclobutyl moiety substituted tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octanes (I)[1] are expected to have a rather high reactivity and a distinct propensity for rearrangements. Recently we reported on the formation of 2(4)-chlorosemibullvalene by fragmentation of the Grignard compounds derived from the trihalogenides Ic and Id[2]:



I

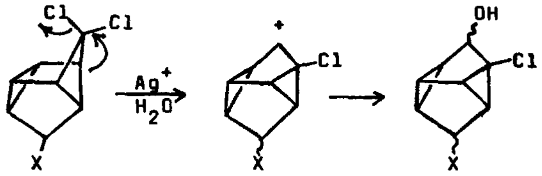
a: X= O-t-Bu
b: X= H
c: X= Br
d: X= Cl



Earlier proposals concerning the formation of trishomocyclopropenyl (II) or bishomo-square-pyramidal (III) carbonium ions from tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane derivatives[3] prompted a study of the cationic behaviour of I.

II

III



Ia,b IVa,b Va,b

In this letter we report that silver ion catalyzed hydrolysis of Ia and Ib[4] does not lead to the products expected from intermediates corresponding to II or III but, instead, yields mixtures of the epimeric tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octan-3-ols (Va: endo-O-t-Bu,endo-OH:endo-O-t-Bu,exo-OH:exo-O-t-Bu,endo-OH:exo-O-t-Bu,exo-OH ca. 37:45:14:4; Vb: endo:exo ca. 3:2)[5]

In our system, which is suitable for both reaction paths, the one leading to cyclobutyl-cyclopropylcarbinyl rearrangement is preferred over the one yielding nonclassical ions like II or III.[6] One reason may be that the nonclassical carbonium ions II and III are destabilized by a chlorine substituent at C-4 more than is IVa,b.[7]

References and comments

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2) P.M. Kwantes, R.F. Schmitz, C. Boutkan, and G.W. Klumpp, Tet. Lett., in press.
3) a) R.M. Coates and K. Yano, Tet. Lett. 1972, 2289; b) A.V. Kemp-Jones, N. Nakamura, and S. Masamune, Chem. Comm. 1974, 109; c) H. Hart and M. Kuzuya, J. Amer. Chem. Soc. 96, 6436 (1974). See also: d) X. Creary, J. Org. Chem. 40, 3326 (1975); e) W. Kirmse and Th. Olbricht, Chem. Ber. 108, 2616 (1975).
4) $AgNO_3/CaCO_3$; dioxane:water 2:1; 45°; 4-5 h; yield: 67%.
5) Separated by gaschromatography, 1.5 m glass column, 15% Carbowax 1540 on Chromosorb W. Structures proved by nmr and by comparison with the *endo*- and *exo*-3-methoxytetracyclo[3.3.0.0^{2,8}.0^{4,6}]octanes[3a] (Va, after removal of chlorine with Li/NH_3 and Jones-oxidation followed by Huang-Minlon reduction) and by conversion of Vb into tetracyclo[3.3.0.0^{2,8}0^{4,6}]octan-3-one[8].
6) Ia,b closely mimics the behaviour of the esters of *endo*-tricyclo[3.2.1.0^{3,6}]octan-4-ol: M. Geisel, C.A. Grob, R.P. Traber, and W. Tschudi, Helv. 59, 2808 (1976).
7) Concerning the substituent effect of (-I,+R)-substituents upon nonclassical carbonium ions, see: P.v.R. Schleyer, P.J. Stang, and D.J. Raber, J. Amer. Chem. Soc. 92, 4725 (1970). In IVa,b chlorine occupies a position, which according to calculations (K.B. Wiberg, Tetrahedron 24, 1083 (1968)) carries the least amount of positive charge.
8) N.A. LeBel and R.N. Liesemer, J. Amer. Chem. Soc. 87, 4301 (1965).

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