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TRANSANNULAR RING EXPANSION OF THE SPIROCYCLOPROPANE MOIETY IN THE ACID CATALYZED REARRANGEMENT OF OXIRANES DERIVED FROM NORBORNENE AND BICYCLO[2.2.2]OCTENE.

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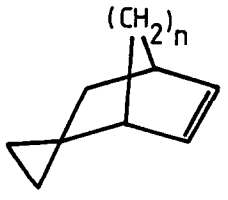
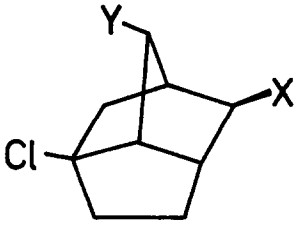
SUMMARY: Treatment of the spirocyclopropane derivatives of epoxy norbornane 5 and epoxy bicyclo[2.2.2]octane 6 with trifluoroacetic acid and perchloric acid affords the substituted brendanes 7 and 9 and homobrendanes 8 and 10 respectively.

The electrophilic addition of arenesulfenyl chlorides to spirocyclopropanenorbornene 1 (n = 1) gave the brendane derivatives 3a,b.[1] This novel rearrange-



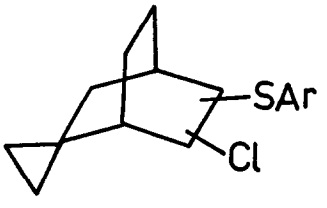
1 (n=1)

2 (n=2)



3a (X=SAr; Y=H)

3b (X=H; Y=SAr)

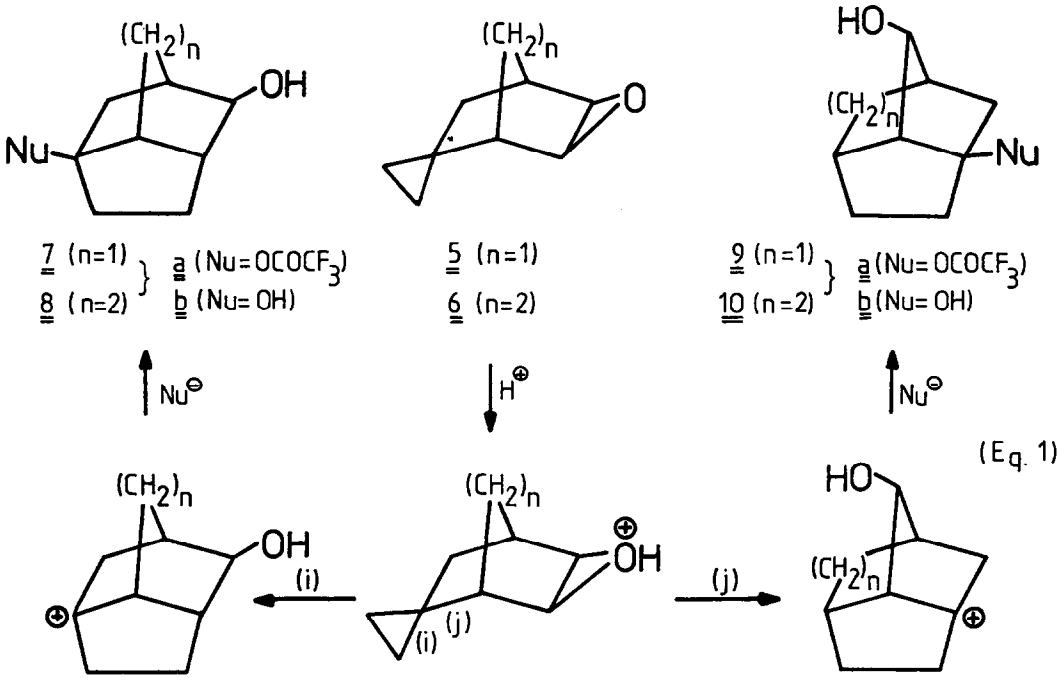


4

ment involving transannular ring expansion of the spirocyclopropane group was to be extended to the corresponding bicyclo[2.2.2]octenes 2 (n = 2), in the hope of providing an efficient synthetic entry into complex carbon skeletons such as the homobrendanes. Unfortunately, with p-toluenesulfenyl chloride the spirobicyclo[2.2.2]octene 2 led exclusively to the addition products 4. Presumably the intermediary episulfonium ion of 2 is trapped by the nucleophilic chloride ion faster than transannular ring expansion of the spirocyclopropane moiety. To promote such neighboring group participation, acid catalyzed rearrangement of the corresponding oxiranes 5 and 6 was employed, anticipating that under these conditions nucleophilic trapping of the protonated oxiranes would be subordinate to transannular ring expansion (Eq.1). Furthermore, besides extending the scope of this novel transannular ring expansion[1], functionalized brendanes 7 and 9 and homobrendanes 8 and 10 would be conveniently made available from simple and readily accessible spirocyclopropane-substituted bicyclic precursors.

The oxiranes 5 and 6 were prepared via epoxidation of the respective olefins 1 and 2 by means of m-chloroperbenzoic acid.[2] The spiroolefin 2 was conveniently prepared via cycloaddition of methylenecyclopropane with 1,3-cyclohexadiene.[2]

Treatment of oxirane 5 with trifluoroacetic acid in CCl_4 afforded the isomeric hydroxy esters 7a and 9a in a 28 : 72 ratio (by capillary GC), while with dilute perchloric acid in H_2O only (by ^{13}C-NMR) the diol 9b was obtained (Eq.1). These proposed structures are consistent with the ^1H- and ^{13}C-NMR spectral data; additionally, an X-ray analysis [3] of the 3,8-diol 9b rigorously established the structural assignment. Furthermore, the hydroxy esters 7a and 9a were separated by flash chromatography on silica gel, eluting with 6 : 1 petroleum ether (30-70)/ethyl acetate and hydrolyzed with KOH/H_2O in ethanol to the respective diols 7b and 9b.[2]



(Eq. 1)

It is of mechanistic import to note that in the arenesulfenyl chloride addition to the spiroalkene 1 mainly transannular ring expansion without skeletal rearrangement (path i in Eq.1) took place, in the trifluoroacetic acid catalysis of the epoxide 5 skeletal rearrangement followed by transannular ring expansion (path j in Eq.1) predominated, while in the perchloric acid catalysis of epoxide 5 path j occurred exclusively. This interesting trend in the product partitioning between path i and j speaks for a more active initial cationic intermediate in the acid catalyzed reaction of the epoxide 5 compared to the arenesulfenyl chloride addition to the spiroalkene 1. Consequently, we expected that transannular ring expansion would be likely in the acid catalyzed transformation of epoxide 6.

Treatment of the exo-epoxide 6 with trifluoroacetic acid in CCl_4 produced the isomeric hydroxy esters 8a and 10a in a 26 : 74 ratio (by capillary GC). Flash chromatography on silica gel, eluting with CH_2Cl_2 led to the pure hydroxy esters 8a and 10a. These were subsequently hydrolyzed with KOH/H_2O in EtOH to the diols 8b and 10b.[2] On the other hand, the endo-isomer gave a complex product mixture (at least ten components by capillary GC). No efforts were made to characterize these because 400 MHz ^{1}H-NMR spectroscopy revealed that essentially all of the spirocyclopropane moiety was still present in the complex product mixture. Skeletal rearrangement leading to a cyclopropylcarbinyl cation and subsequent transformations of the latter readily account for this product complexity of the endo-epoxide 6.[4] Thus, for transannular ring expansion to take place, either with (path i) or without (path j) skeletal rearrangement, an antiperiplanar arrangement of the participating bonds (exo-isomer of epoxide 6) appears to be essential.

For both epoxides 5 and 6 examined here, acid catalyzed treatment proceeds mainly via path j (Eq.1), affording the rearranged products 9 and 10. Skeletal rearrangement [5] takes place prior to transannular ring expansion of the spirocyclopropane. Competing with this route is path i (Eq.1), leading to the products 7 and 8 via transannular ring expansion prior to skeletal rearrangement. Thus, the functionalized brendanes and homobrendanes, complex tricyclic structures, can be made conveniently from the readily accessible epoxides 5 and 6 by treatment with protic acids.

ACKNOWLEDGEMENT

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2. All new compounds were fully characterized by means of elemental analyses and spectral data. The experimental details will be reported in the full paper on this subject. The yields given below refer to isolated pure products. Product balance in the acid catalyzed reactions was in each case better than 80 %.

Spiroolefin 2: 50%; colorless liquid, b.p. 80 °C at 18 Torr.

Oxirane 5: 26%; colorless oil, b.p. 80–90 °C at 0.1 Torr (Kugelrohr).

Oxirane 6: 77%; colorless oil, b.p. 60–70 °C at 0.1 Torr (Kugelrohr); a ca. 2 : 1 mixture (by GC on a 1.5 m x 8 mm column, coated with 10% Carbowax M on Chromosorb WHP, operated at 90 °C column temperature and a 0.3 kg/cm² N_2 flow rate) of exo- and endo-isomers was produced.

Hydroxy ester 7a: 4%, colorless oil, b.p. 120–130 °C at 0.1 Torr (Kugelrohr).

Hydroxy ester 9a: 10%, colorless oil, b.p. 110–120 °C at 0.1 Torr (Kugelrohr).

Diol 7b: 52% from hydrolysis of hydroxy ester 7a; colorless needles, m.p. 232–233 °C (1 : 1 petroleum ether (30–70)/ethyl acetate).

Diol 9b: 51% from hydrolysis of hydroxy ester 9a; colorless prisms, m.p. 254–255 °C (ethanol).

Hydroxy ester 8a: 16%; colorless wax, 150–160 °C/0.1 Torr (Kugelrohr).

Hydroxy ester 10a: 46%; colorless plates, m.p. 82–83 °C (methylene chloride).

Diol 8b: 80% from hydrolysis of hydroxy ester 8a; colorless needles, m.p. 163–164 °C dec. (chloroform).

Diol 10b: 31% from hydrolysis of hydroxy ester 10a; colorless needles, m.p. 205–208 °C dec. (chloroform).

3. Run for us by Dr. K. Peters (Stuttgart); the details of the structural data will be provided in full paper on this subject.

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