DIRECTED SYNTHESIS OF <u>EXO</u>, <u>ENDO</u> - BISHOMOBARRELENE[*] AND TRISHOMO-BARRELENE[*]

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Bridgehead chlorides of trishomobarrelene and trishomobullvalene have revealed an unprecedented solvolytic reactivity[1,2]. Continuing interest in these remarkable model systems has lead us to prepare several other bridgehead derivatives including the carboxylic acids, alcohols and methyl ethers[2,3]. However, the unavailability of trishomobarrelene and trishomobullvalene on a larger scale has so far precluded a study of their bridgehead reactions on a broad scope.
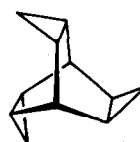
We now wish to report a new convenient preparation of monohomobarrelene (<u>1</u>) as well as a directed synthesis of <u>exo</u>, <u>endo</u>-bishomobarrelene (<u>2</u>) and trishomobarrelene, which makes this series of hydrocarbons readily available in 20 to 50 g quantities.
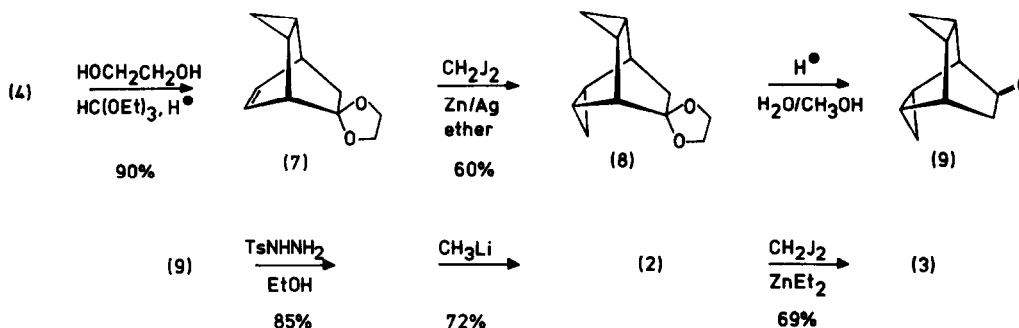

(1)   (2)   (3)

Tricyclo[3.2.2.0^{2,4}]non-6-en-9-one (<u>4</u>) can be prepared in three steps with reasonable yield from cycloheptatriene and acrylonitrile[4]. The tosylhydrazone (<u>5</u>) obtained from (<u>4</u>) and tosylhydrazide in ethanol (85 % yield), was reacted with two equivalents of methyllithium in dry ether[5] and gave (<u>1</u>) in 77 % yield. This procedure is superior to published preparations of (<u>1</u>)[6,7], because the overall yield (32 % based on 8-cyano-tricyclo[3.2.2.0^{2,4}]nonene-6) is higher[6] and it can be scaled up without difficulty[7,8].
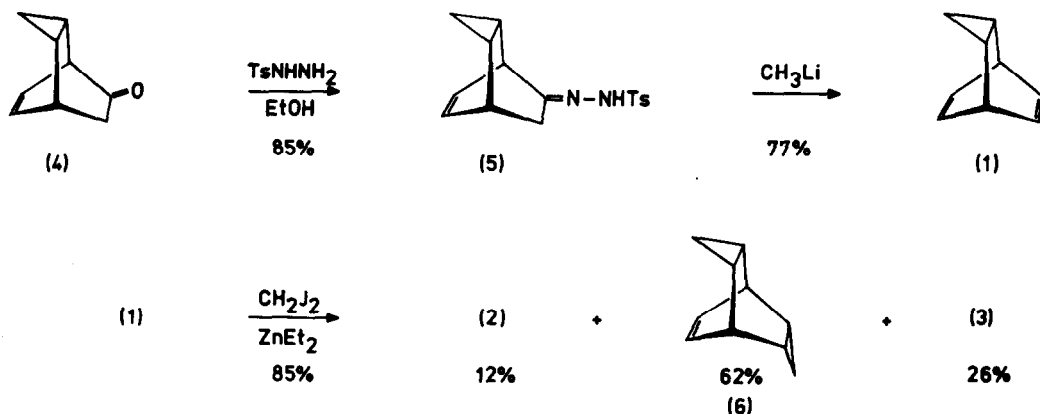
The cyclopropanation of (1) with diazomethane/cuprous chloride as reported[9]

yields a mixture of exo, endo-(2) and endo, endo-bishomobarrelene (6) along

with trishomobarrelene (3). The modified Simmons–Smith reaction with methy-

lene iodide and diethylzinc[10] when applied to (1) leads to a similar mixture

of (2) (12 %), (6) (62 %) and (3) (26 %) in 85 % total yield. The yield of

(3) obtained in this way is 22 % based on (1), the largest proportion of

starting material reacts to (6), which for steric reasons, cannot undergo

further methylene addition to form a trishomobarrelene stereoisomeric with (3).

This disadvantage, however, can be overcome by a directed stepwise addition

of two methylene groups onto the skeleton of (1). For instance, the cyclopro-

panation of (4) could only give one isomer of tetracyclo[$3.3.2.0^{2,4}.0^{6,8}$]-

decan-10-one (9). Unfortunately, (4) did not react with methylene iodide/zinc-

copper couple, although the Simmons–Smith reaction has successfully been used

on a number of α,β-unsaturated ketones[11]. Ketalization of the carbonyl group

was found to be necessary in this case (90 %)[12]; the ethylene ketal (7)[13]

then reacted in the expected way to form (8)[13,14] (60 %), which upon hydro-

lysis gave exo, endo-tetracyclo[$3.3.2.0^{2,4}.0^{6,8}$]decan-10-one (9)[13] (87 %

yield). The tosylhydrazone of (9) (85 %) was reacted with methyllithium in

dry ether in the same way as (5) to give pure exo, endo-bishomobarrelene (2)

in 72 % yield.

Further cyclopropanation of (2) can now only lead to (3). In this case the reaction with methylene iodide and diethylzinc[10] was found to give the best yields: 69 % (3) and 16 % (2) recovered, applying a threefold excess of the reagents. (2) could conveniently be separated from the mixture resulting in this procedure by vacuum distillation, through a 30 cm concentric tube col-

umn[15], the remaining (3) was finally purified by sublimation under reduced pressure, thus allowing the isolation of 20 to 50 g quantities in one batch. Distilled (2), b. p. 66°C, 12 Torr and sublimed (3), m. p. 56 – 57°C had NMR-spectra identical to those obtained for gaschromatographically purified samples, their purity as tested by analytical g. c. was found to be 98 % and > 99 % respectively.

References and footnotes

[*] Systematic names: exo, endo-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]decene-9 and pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane respectively.

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8) In our hands, the anodic oxydative bisdecarboxylation of tricyclo[3.2.2.
    $0^{2,4}$]non-6-en-9,10-dicarboxylic acid in aqueous pyridine[7] gave at best
    10 - 15 % yields (isolated). In addition, the electrolysis could only be
    run on a small scale (3 - 6 g of the dicarboxlic acid)[7].

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     Tetrahedron Lett., 3495 (1968)

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12) Alternatively, (4) was reduced with lithium aluminium hydride to a mix-
     ture of exo- and endo-tricyclo[3.2.2.0^{2,4}]non-6-en-9-ol; in this mixture
     only the endo-isomer was readily cyclopropanated with methylene iodide/
     zinc-copper couple, subsequent reoxidation then gave a mixture of (4)
     and (9), the yield of (9) (based on (4)) being about 50 % lower than in
     the other procedure.

13) All new compounds gave satisfactory elemental analysis data.

14) Here and in other cases we have made use of a modified Simmons-Smith
     procedure, cf. J. M. Denis, C. Girard and J. M. Conia, Synthesis 3,
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