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SYNTHESIS OF *ANTI*-1,2-DI(7'-NORCARANYLIDENE)CYCLOPROPANE

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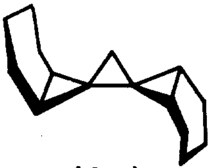
There has been considerable recent interest in polyspiranes containing two or more cyclopropane rings from theoretical and synthetic viewpoints.[1] More recently, the synthesis of the first silacyclopropane (1) has been presented by Seyferth *et al.* and, interestingly, the structure of 1 has been determined to be *anti*-form by means of X-ray analysis and ^{13}C NMR study.[2] In this connection, we now wish to report the synthesis of the hydrocarbon analog of 1, that is, *anti*-1,2-di(7'-norcaranylidene)cyclopropane (2a).

(1)

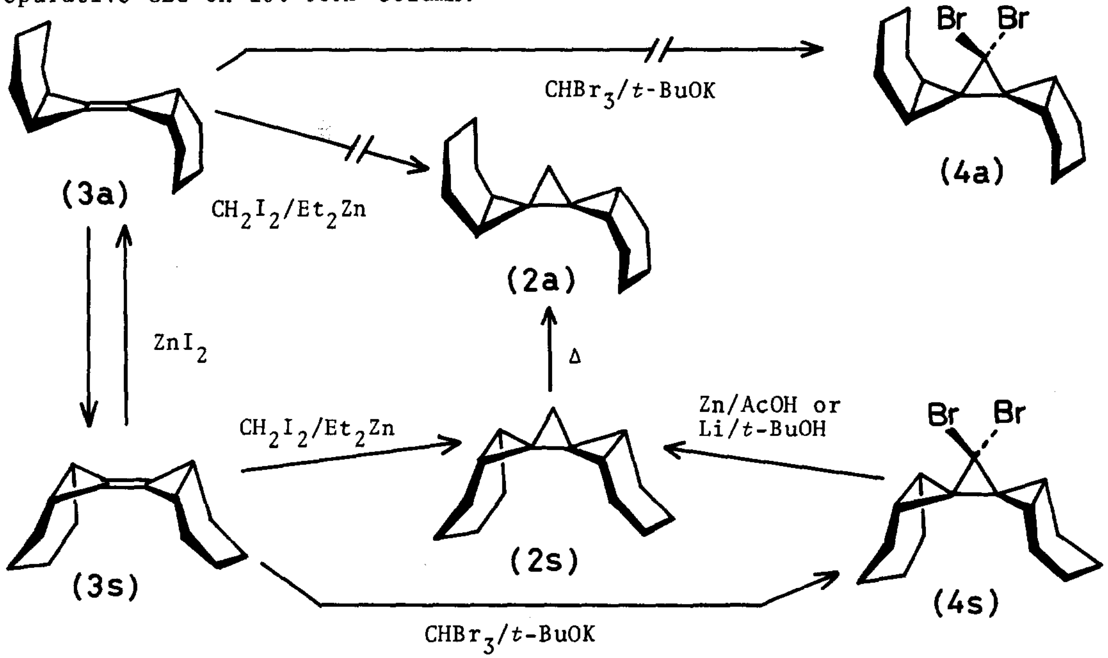


(2a)

Treatment of 7,7-dibromonorcarane with MeLi in ether at -90°C[3] afforded an 1:10 mixture of two isomers [*anti* (3a) and *syn* (3s)][4] in 40% yield. In order to obtain large enough amount of 3a to be usable for later reaction, the catalyzed isomerization[5] of 3s to 3a with ZnI_2 was carried out and the *anti/syn* ratio of the mixture was improved up to 1:2 at equilibrium.

Unfortunately, the cyclopropanation of 3a with 2 molar excess of Et_2Zn and CH_2I_2 according to the Furukawa's method[6] did not give the desired *anti*-dispiro cyclopropane (2a) at all but rather 3s resulting from rapid isomerization because of the catalysis of ZnI_2 generated *in situ* in this reaction. Furthermore, an attempt to prepare 4a, as a requisite precursor, by addition of dibromocarbene to 3a was unsuccessful on account of unexpectedly large steric hindrance of cyclohexane rings toward addition.

The present difficulty could be overcome by the thermal geometrical isomerization[7] of *syn*-isomer (2s) which was easily obtained by the same cyclopropanation as mentioned above in 92% yield and was also given by dehalogenation of *gem*-dibromocyclopropane (4s) [m.p. 180-182°C], which was formed by addition of dibromocarbene to 3s in 76% yield, with Zn/AcOH or Li/*t*-BuOH in 93% or 86% yield, respectively. Thermal reaction of 2s was carried out in the N_2 flow system at 340-390°C for periods ranging from 20 to 160 s. One portion (1 ml) of a *n*-hexane solution of 2s was conducted with N_2 gas (10-100 ml/min) into the Pyrex thermal reactor and the desired 2a was given in 45% yield under the best condition (370°C, 40 s), which was purified by preparative GLC on 10% FFAP column.



The structure of 2a was supported by the off-resonance ^{13}C NMR spectrum which showed 2 singlets (δ 20.9 and 21.4), 2 doublets (δ 10.1 and 15.1), and 5 triplets (δ 9.8, 21.2, 21.8, 21.9, and 22.1) in contrast with that of 2s which showed only one singlet (δ 25.1), one doublet (δ 17.2), and 3 triplets (δ 18.0, 21.5, and 22.9).

The further investigation on the reactivity of 2a and 2s in thermal reaction or catalytic reaction is in progress.

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