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SYNTHESIS OF POLYCYCLIC ALKENES *VIA* REDUCTIVE ELIMINATION OF ß-DICYANO DERIVATIVES: A FACILE PREPARATION OF *ANTI*-SESQUINORBORNENE AND RELATED MOLECULES

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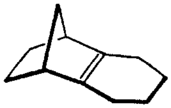
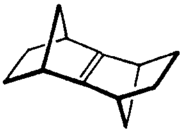
Summary: *Anti*-Sesquinorbornene **1b**, the hitherto unknown related unsaturated molecules **1a,c** and the dienes **13** and **14** are among the endocyclic alkenes which can be prepared *via* reductive elimination of the respective, readily available ß-dicyano derivatives.

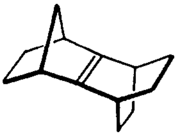
The synthesis of polycyclic alkenes of the type sesquinorbornenes,[1] despite the recent improvements,[2] is still rather difficult. Nonetheless these molecules are receiving much attention because of their peculiar geometric and electronic features.[3]



(**1a**)



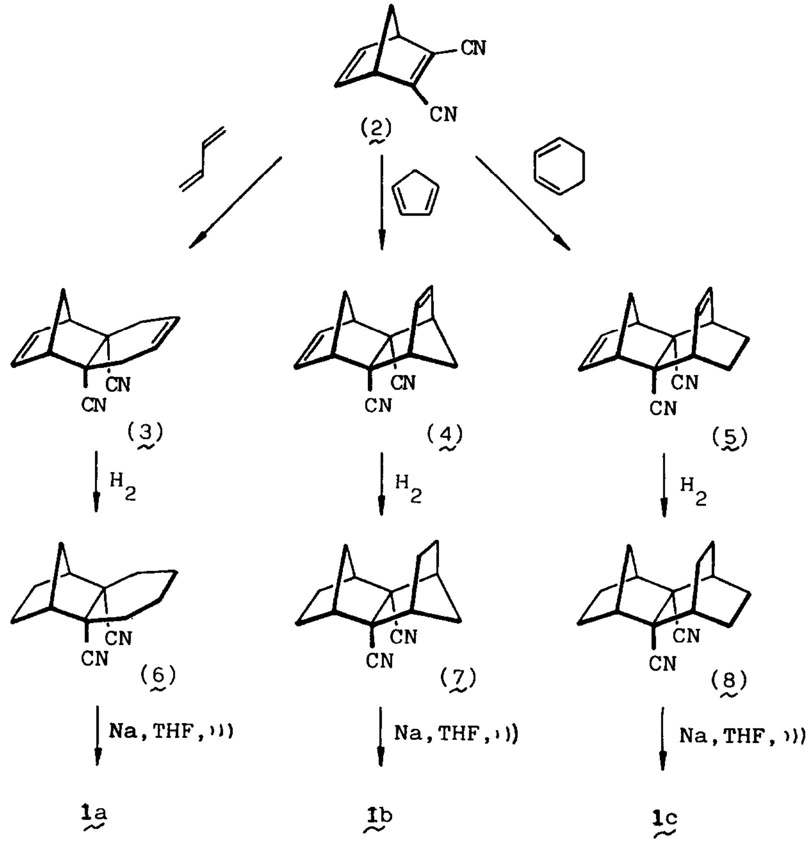
(**1b**)



(**1c**)

In connection with our work on the synthesis of new polycyclic molecules *via* reductive methods,[4] we report here a rapid and simple method for the preparation of *anti*-sesquinorbornene (**1b**). The method can be expanded to the preparation of homologues and other related molecules hitherto unknown perhaps because of the unsuitability of the reported synthetic procedures which are based on oxidative processes.

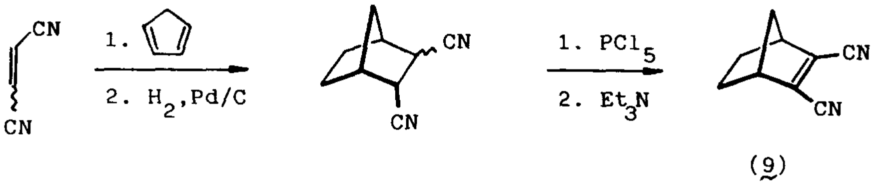
On heating 2,3-dicyanonorbornadiene **2**[5] with butadiene (generated *in situ* from 3-sulfolene) at 120°C for 24 h,[6] a *ca.* 4:1 mixture of the corresponding *exo* and *endo* Diels-Alder adducts (**3**) is obtained in 45% yields[7] (*exo*-**3**: mp 176-178°C with decomposition from MeOH). The adduct of cyclopentadiene, **4** (colorless crystals from dichloromethane-petrol ether; melting point with decomposition over 170°C), can be obtained in one pot by mixing a dichloromethane solution of dicyanoacetylene with excess cyclopentadiene at room temperature for few days. The product is almost purely the anti isomer. Alternatively, **4** can be prepared in 48% yield[7] in a sealed vial at 120°C for 12 h. The adduct of 1,3-cyclohexadiene is obtained in 15% yield[7] in the latter conditions and it is formed as a ca. 6:1 mixture of isomeric alkenes.[6]



To the best of our knowledge, the addition of two molecules of cyclopentadiene to dicyanoacetylene, although it is already known for related alkynes,[1,8] has not been previously reported. Similarly, there are no cases known in which dicyanoacetylene has been added to two different dienes as it is in the case of adducts **3** and **5**.

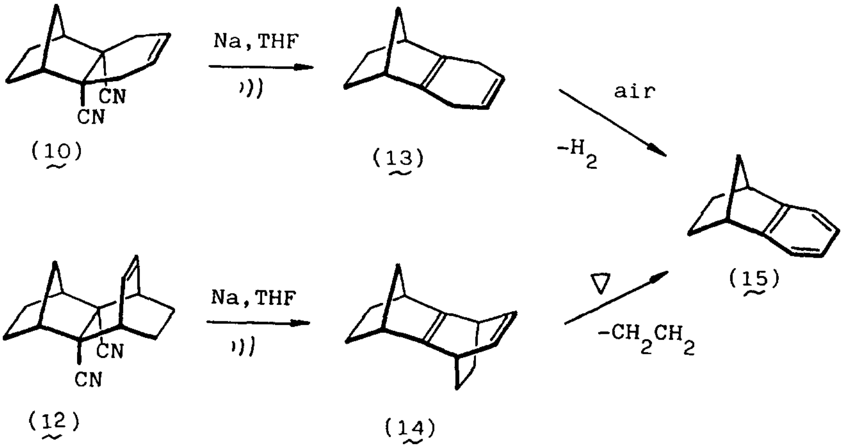
Reduction of **3-5** with hydrogen and 5% palladium on carbon affords in quantitative yields the saturated compounds **6-8** as crystalline solids (**6**: mp 132-134°C (CH_2Cl_2/petrol ether); **7**: mp 166°C (MeOH); **8**: mp 193-196°C (MeOH)). These ß-dicyanoderivatives on treatment with sodium sand in refluxing tetrahydrofurane, in a sonicator for 15-20 minutes, produce the respective alkenes **1a-c**, as shown by their 'H-NMR and mass spectra, in more than 30% yield.

Because the moderate yields in the cycloaddition reactions are due to retro-Diels-Alder processes or to addition to the unactivated double bond, these reactions have been repeated with improved yields starting from 2,3-dicyanonorbornadiene 9[9] (74, 60 and 43% yields[7] and mp 181-182°C (CH_2Cl_2/petrol ether), 155-158°C (MeOH), and 186-187°C (MeOH) respectively for the cycloadducts of butadiene **10**, cyclopentadiene **11** and 1,3-cyclohexadiene **12**). Dienophile **9** can be synthesized in high yields by selective hydrogenation of **2**, or much more conveniently from the sequence of reactions of equation 1[10] from which it can be readily obtained in multigram quantities from commercially available reagents. Furthermore cycloadditions to **9** show a higher stereoselectivity than that to **2**. Standard hydrogenation of **10–12** affords quantitatively **6–8**.



(1)

Unsaturated ß-dicyanoderivatives can also be reductively decyanated. For example, **10** and **12** (derived from cycloaddition of butadiene and 1,3-cyclohexadiene to **9**) give dienes **13** and **14** in ca. 30% yields.[11] They both are transformed to benzonorbornene **15**, the former by air oxidation and the latter via a thermal retro Diels-Alder elimination of ethylene.



Although the yields in the elimination step are not high, the present way of reductive decyanation with sodium sand in tetrahydrofuran is in our opinion easier and safer than other known methods[12] and it is the only way which gives alkenes uncontaminated with overreduced products. The overall procedure for the synthesis of **1b** compares well with the known preparations[1,2] as far as stereoselectivity, yields and the facility of operations are concerned. Furthermore, the present method has a wider scope.

Grateful thanks are due to Dr. Giulia Licini for preliminary experiments on the sesquinorbornenes.

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6. On prolonged heating there are also formed products derived from retro Diels-Alder processes and/or of addition to the unactivated double bond. In the case of 1,3-cyclohexadiene, there are also formed benzene, hydrogenated products and a small amount of quinoline.

7. Yields are based on recovered starting material with a conversion range of 70-90%. All new compounds present correct composition by combustion analysis.

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11. The cycloadduct derived from **9** and cyclopentadiene failed however to give the expected sesquinorbornadiene. The latter has recently been prepared via an other route (L.A. Paquette, H. Kuenzer, K.E. Green, O. De Lucchi, G. Licini, L. Pasquato, and G. Valle, submitted to publication).

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