contrast, addition of either triflate **7a** or **7b** to cyclohexene as substrate results in formation of the respective dimers **11a** and **11b** via **9**. Products **10, 11a,** and **11b** were characterized and identified by spectral means as summarized in Table I. These spectral properties are completely consistent with the proposed structures. The medium-intensity 2065-cm^{-1} band and the 264-nm λ_{max} of **10** are indicative of cumulenes.[9] The intense low wavelength absorption (202- and 207-nm λ_{max}, respectively) for both **11a** and **11b** is characteristic of known radialenes as is the weak 1710-cm^{-1} band.[10] The ^{1}H NMR are also consistent with the proposed structures, although they do not differentiate between monomer and dimer.

The most characteristic and useful spectral features of **10, 11a,** and **11b** are exhibited by the mass spectra and ^{13}C NMR data. For both **10** and **11b**, the respective molecular ions are the base peaks and, for **11a**, the molecular ion has an intensity of 94%. The ^{13}C spectrum of **10** is in accord with those of analogous cumulenes[11] and the spectra of dimers **11a** and **11b** are characteristic of similar alkylidenecyclopropanes[12] and in harmony with expectations[13] for such hydrocarbons.

In summary, we have discovered a simple highly efficient means of allenylidene carbene **4** generation. These species readily add to olefins to give highly oxygen sensitive cumulenes and their dimers. At present, we are examining the possibility that allenylidene carbenes **4** are similar in nature to the related unsaturated carbenes **2** and **3** which are found to be electrophilic and possess a singlet ground state.[14] This question, as well as the chemistry of these novel unsaturated reactive intermediates, will be the subject of future reports.

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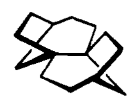
Twofold Cation-Olefin Cyclization. Synthesis of *syn*-[3.2.1]^2- and [2.2.2]^{2}Geminane

Sir:

A large number of topologically fascinating molecules constructed of repeating alicyclic units are possible. Of these, only the homologous series comprised of adamantane,[1] diamantane,[2] triamantane,[3] and the tetramantanes[4] has received significant attention. This is a consequence not only of their relationship to the diamond lattice,[5] but also because of their relative thermodynamic stability and consequent ready availability by Lewis acid catalyzed cationic rearrangement of many isomeric precursors.[6] Since this synthetic approach is not extrapolatable to ring systems having different topographies, the absence of molecules from the latter group can be traced chiefly to an existing lack of viable synthetic methodology.[7,8] In this communication, we outline a new approach within this field of research which is founded on the concept of twofold cation-olefin cyclization, and is both efficient and simple. The present contribution describes the synthesis of novel hydrocarbons **1** and **2** which, for convenience, have been colloquially named *syn*-[3.2.1]^{2}geminane and [2.2.2]^{2}geminane, respectively.[9,10]



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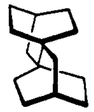
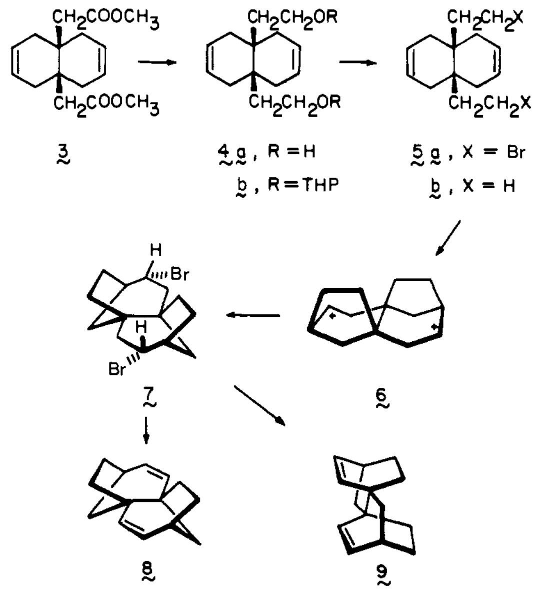


2

The molecular frameworks of **1** and **2** are formally constructed of pairs of bicyclo[3.2.1]octane and bicyclo[2.2.2]octane ring systems, respectively, which have been fused symmetrically across a common C_1–C_2 bond. This innovation delivers a C_2 symmetric structure for **1** and a still more symmetric (C_{2h}) molecule in the case of **2**.

Reduction of known diester **3**[11] with lithium aluminum hydride in refluxing tetrahydrofuran afforded diol **4a** (98%), mp 152–153 °C,[12] which was subsequently converted to the bistetrahydropyranyloxy derivative **4b** (100%). Treatment of **4b** with triphenylphosphine dibromide in dichloromethane at room temperature for 20 h led directly[13] to dibromide **5a** (67%): mp 133.5–134.5 °C; ^{1}H NMR (δ, CDCl$_3$) 5.46 (narrow m, 4 H), 3.28 (t, J = 7 Hz, 4 H), 1.98 (pseudosinglet, 8 H), 1.97 (t, J = 7 Hz, 4 H). For subsequent comparison purposes and to further substantiate that **5a** had formed without rearrangement, the dibromide was reduced with sodium in liquid



ammonia (or alternatively $LiAlH_4$ in THF) to give oily hydrocarbon **5b:**[12] ^{1}H NMR (δ, $CDCl_3$) 5.26 (narrow m, 4 H), 1.90 (pseudosinglet, 8 H), 1.46 (q, J = 6.5 Hz, 4 H), 0.78 (t, J = 6.5 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 125.06, 36.27, 31.36, 23.84, 7.91.

While **5a** was stirred with approximately ten times its weight of silica gel (activity I) in petroleum ether (30-60 °C) at room temperature for 48 h, the reaction mixture was seen to progress through several color changes (colorless → yellow → orange → red).[14] Filtration and concentration of the reaction mixture delivered **7** (83%): mp 182.5-183.5 °C;[12] ^{1}H NMR (δ, $CDCl_3$) 4.33 (m, 2 H), 2.67-0.90 (series of m, 18 H). The high regioselectivity of the intramolecular neighboring π-bond participation to give **6** (synchronous formation of dication not implied) is striking, particularly in view of literature precedent involving bicyclo[3.2.1]octanyl-bicyclo[2.2.2]octanyl interconversions[15] and other observations to follow. That the stereochemistries about the bromine substituted carbon atoms must be identical follows from the simplified ^{13}C NMR spectrum (57.19, 46.66, 42.72, 40.05, 38.16, 33.94, 30.29 ppm) which requires C_2 symmetry. The *syn*-methano configuration was deduced from steric considerations (see **6**), ^{1}H NMR analysis, and subsequent reactions.

As expected, reduction of **7** with tri-*n*-butyltin hydride gave **1**, a colorless solid: mp 78.5-79.5 °C;[12] ^{13}C NMR (ppm, $CDCl_3$) 47.68, 40.20, 36.36, 34.86, 32.43, 30.97, 28.26.

Access to dienes **8** and **9** can be gained by various routes. For example, exposure of **7** to silver perchlorate in benzene-pentane solution, potassium *tert*-butoxide in tetrahydrofuran, or basic alumina (slurry in petroleum ether) afforded mixtures of the two hydrocarbons. In more expeditious fashion, direct treatment of **5a** with silver perchlorate or simply with basic alumina also gave these products. In every instance, **8** dominated the composition at the 65-75% level. The dienes were separated by high-pressure liquid chromatography on silica gel. Diene **8** is a colorless solid: mp 76.5-77.5 °C;[12] ^{1}H NMR (δ, $CDCl_3$) 5.73 (dd, J = 10, 6 Hz, 2 H), 5.06 (d, J = 10 Hz, 2 H), 2.45-1.14 (series of m, 14 H); ^{13}C NMR (ppm, $CDCl_3$) 135.01, 132.73, 51.85, 42.77, 36.31, 33.89, 31.70. Diene **9** is equally crystalline and stable: mp 99.5 °C (sealed tube);[12] ^{1}H NMR (δ, $CDCl_3$) 5.67 (dd, J = 10, 7 Hz, 2 H), 5.20 (d, J = 10 Hz, 2 H), and 2.55-0.66 (series of m, 14 H); ^{13}C NMR (ppm, $CDCl_3$) 134.19, 130.94, 51.61, 38.21, 37.58, 35.88, 33.26.

Catalytic hydrogenation of each of these purified dienes over platinum in ethyl acetate solution gave **1** and **2.** The high symmetry of **2,** mp 72.0-72.5 °C,[12] is apparent from its five-line decoupled ^{13}C NMR spectrum (ppm, $CDCl_3$: 43.50, 34.52, 33.06, 31.22, 28.94).

The tactical use of twofold cation-olefin cyclization in the manner herein described promises to be of some generality. Given the wide diversity of possible starting materials, the methodology can serve as a useful conceptual template for the elaboration of manifold polycondensed systems.[16]

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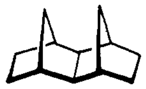
(9) Dr. Kurt Loening of Chemical Abstracts Service has informed us that the correct systematic names for **1** and **2** are octahydro-3*H*,8*H*-3,5a:8,10a-dimethanoheptalene and octahydro-2,4a:6,8a-diethanonaphthalene. In the von Baeyer system, the names of the molecules are less readily distinguishable (tetracyclo[8.2.1.1^{4,7}.0^{1,7}]tetradecane vs. tetracyclo-[6.2.2.2^{3,6}.0^{1,6}]tetradecane), although the actual number of rings is now made quite evident. To facilitate conversation, we propose the generic name geminane (*L.* geminus, twin) for that class of compounds having *two identical bicyclic ring systems mutually fused across a bond involving a bridgehead carbon from each segment.* The basic nature of the constituent rings would then be expressed numerically in the usual way within suitable brackets, with the fused bridge given precedence. Since the sizes of the fused bridges in **1** and **2** are identical, further abbreviation can be achieved by simply squaring the bracket (see title). To denote that bridges of the same size are proximal in **1,** the prefix syn is added. If bridgehead carbon atoms are not involved in the ring fusion as in i, use of the geminane nomenclature would be *inappropriate.* Any necessary numerical designations can be applied on the basis of the systematic number scheme. Accordingly, **9** is [2.2.2]^{2}gemina-1,9-diene, although *syn*-[2.2.2]^{2}-geminadiene would suffice in this instance.



i

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