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Preliminary Communication

Tetra-cycloalkanes. I.

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Tetrahedrane (**1**)[1-4] and adamantane (**4**)[3b,5-7] have been attracting experimental and theoretical chemists for a long time. Both are tetracyclic hydrocarbons with T_d symmetry. Their relationship, however, has not been *fully* recognized as yet.

Tetrahedrane and adamantane have four bridgehead carbon atoms arranged in space at the angles of a tetrahedron and both are »caged« by four equivalent faces, cyclopropanes and cyclohexanes, respectively. Adamantane can be formally derived from tetrahedrane by an insertion of six methylene groups into six bridges of tetrahedrane (Fig. 1). Therefore, adamantane can be considered as a member of a homologous series which begins with tetrahedrane and in which higher members are derived by a successive insertion of two methylene groups into two opposite bridges of tetrahedrane (Fig. 2). Since each member of this homologous series contains four equivalent faces, we suggest the name *tetra-cycloalkanes* (4 x cycloalkane) as the common name for this series of cage hydrocarbons. Consequently, the first seven members may be named as: tetra-cyclopropane (tetrahedrane, **1**), tetra-cyclobutane (**2**), tetra-cyclopentane (bisnoradamantane, **3**) tetra-cyclohexane (adamantane, **4**) tetra-cycloheptane (symm. bishomoadamantane, **5**), tetra-cyclooctane (**6**), and tetra-cyclononane (**7**).

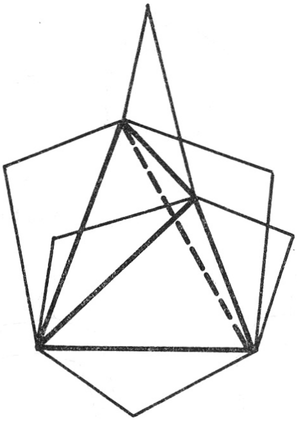

Fig. 1

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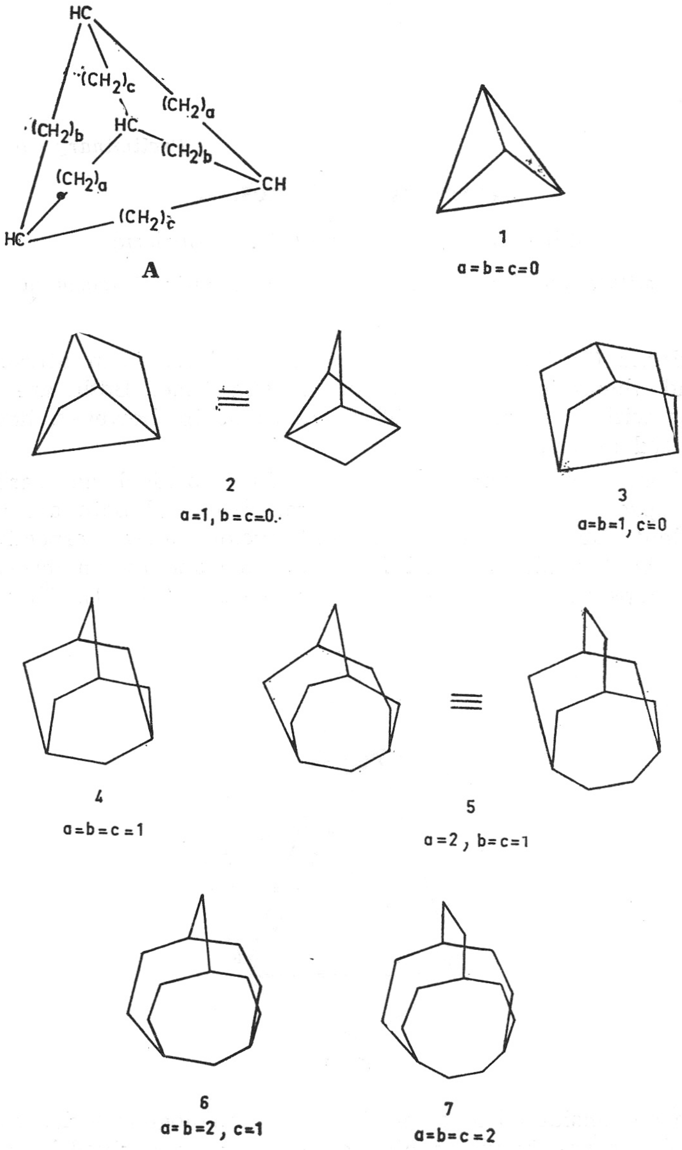

Fig. 2. Tetra-cycloalkanes.

The general formula of tetra-cycloalkanes is C_nH_{2n-4}; four bridgehead carbon atoms are arranged at or nearly at the angles of a tetrahedron and number of carbons in the bridges may be either $a = b = c$ or $a = b$, $c = a \pm 1$ (see Fig. 2, A)*. Such a geometry should be related to both physical and chemical

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* Tetra-cycloalkanes can be considered as a special case of a more complete homologous series (polyhedranes) in which higher members can be formally derived by successive insertion of *one* methylene group into the various bridges of tetrahedrane.

properties which can be expected to be either alike or to change gradually with the increasing number of carbon atoms. Boiling points should be low and melting points high relative to open-chain hydrocarbons. Certain chemical properties are expected to be common for all tetra-cycloalkanes, *e. g.* a steric hindrance to direct displacement and solvent assisted reactions. Many chemical properties, however, should change gradually with the increasing number of carbon atoms, mainly due to increasing stability of bridgehead carbonium ions and free radicals. An important factor is strain.

The first four tetra-cycloalkanes (**1**—**4**) are rigid systems. Higher members (**5**—**7**), however, can accommodate angles in the ethylene bridges to achieve the least strained conformations. Total strain (and stability) in tetra-cycloalkanes should be in the first approximation a balance of three types of strain: *i)* angle strain, resulting from a large deviation of bonds from the tetrahedral angle, *ii)* strain originating from eclipsed or partially eclipsed bonds, and *iii)* transannular strain, due to interactions of the substituents on nonadjacent carbons. Total angle strain is obviously the most important in tetrahedrane (**1**) and tetra-cyclobutane (**2**), being considerably higher in the former*.

A so-called negative angle strain could be expected for tetra-cyclononane (**7**) and higher tetra-cycloalkanes since some of the transannular strain and the strain due to eclipsed bonds may be relieved in large rings by the adoption of bond angles larger than ~ 110°. The last two types of strain contribute largely to the strain in the medium ring tetra-cycloalkanes (**3**—**6**), having a minimum for adamantane**, which is practically free of all three mentioned types of strain[5a]. Recent calculations[6], however, showed that adamantane is strained 6.5 kcal/mol relative to »single-conformation« group increments. This strain originates from the »hard« C . . . . C and H . . . . H nonbonded repulsions from which the rigidity of the adamantane skeleton allows no escape[6]. The same type of strain may be considerably more important for the lower tetra-cycloalkanes (**1**—**3**), reaching a maximum for tetrahedrane, and sharply decreasing in the higher tetra-cycloalkanes (**5** → **7**).

The relative total strain in tetra-cycloalkanes can be expected therefore to be at a minimum for adamantane and to increase sharply towards the lower and less sharply towards the higher members of the homologous series. Consequently, the higher tetra-cycloalkanes are to be expected to rearrange into adamantane derivatives under proper conditions (*e. g.* AlX_3 catalysis) while the lower members could relax their strain only by a ring opening and rearrangement into »less caged« systems.

The available experimental data, though scarce, are in accord with these conclusions. The tetrahedrane system has never been successfully prepared[1], although **1** was claimed recently as an excited intermediate in the reaction of cyclopropene with $:C:C:O$ leading to acetylene[2]. Numerous theoretical calculations[3,4] predict a high strain ($>$ 150.5 kcal/mole)[4] for **1** and indicate that **1** should be very unstable at room temperature[4]. Tetra-cyclobutane (**2**) and the higher homologs, tetra-cycloheptane, tetra-cyclooctane and tetra-cyclo-

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* Total angle strain is approximatively 297° in **1**, 137° in **2**.

** An inspection of the models indicates a decreasing of these types of strain in the order: $\mathbf{3} > \mathbf{5} \approx \mathbf{6} \gg \mathbf{4}$.

nonane (**5**—**7**), are unknown systems*. However, the tricyclo [2.1.0.0.^{2,5}] pentane system, which is related with **2**, but is more strained, has been successfully prepared[8]. Tetra-cyclopentane (**3**) and some derivatives have been reported recently[9]. Strain in this system is demonstrated by solvolysis of the secondary chloride and *p*-bromobenzenesulfonate of **3**, which lead completely rearrangement to the more stable tricyclo [3.2.1.0^{3,6}] octane system[10]. Tetra-cycloheptane (**5**) should have a strain comparable to that of homoadamantane, which is known[11] to rearrange readily into adamantane derivatives in the presence of AlX_3. Adamantane (**4**) is a very stable system[5,12] and by far the best known of all tetra-cycloalkanes**,[5]. In the presence of Lewis acid catalyst all tricyclodecanes investigated to date have rearranged completely to adamantane[5,12], indicating that adamantane is at *least* 5—6 kcal/mol more stable than any of its isomers[12].

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* Synthesis and extensive studies of chemistry of these systems (**2** and **5** in particular) are currently under way in our laboratory.

** A whole new branch of chemistry was developed on the basis of adamantane in the last 15 years!

IZVOD

Tetra-cikloalkani I.

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Tetrahedran se može smatrati prvim članom homolognog niza tetra-cikloalkana. Viši članovi formalno se mogu izvesti postepenim umetanjem po dvije metilenske grupe u dva suprotna mosta tetrahedrana. Kemijska svojstva usko su vezana s ukupnom napetošću. Ukupna napetost najniža je kod adamantana i postepeno raste prema nižim (brže) i višim (sporije) članovima homolognog niza.

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