

Metal Complex Catalysis in the Synthesis of Strained Polycyclic Hydrocarbons

R. I. KHUSNUTDINOV

Institute of Petrochemistry and Catalysis, Ufa Scientific Centre of the Russian Academy of Sciences, Pr. Oktyabrya 141, Ufa 450075 (Russia)

E-mail: ink@anrb.ru

Abstract

Literature data are generalized devoted to developing one-stage methods for the synthesis of strained polycyclic hydrocarbons with the use of metal complex catalysts. These methods are based on the reactions of homo- and cross-cyclization of norbornadiene and its derivatives with olefins, 1,2-dienes, 1,3-dienes and acetylenes. Using these reactions the synthesis has been performed to produce tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-, undeca- and dodecacyclic strained hydrocarbons difficult to obtain by means of other methods.

Key words: metal complex catalysis, strained polycyclic hydrocarbons, cycloaddition, norbornadiene, olefins, 1,2-dienes, 1,3-dienes, acetylenes

For the recent years complicated strained polycyclic hydrocarbons (SPH) appeared the object of the most steadfast attention by chemists engaged in synthesis. An increased interest with respect to such compounds is caused by an originality of their structure as well as by valuable practical significance. Strained polycyclic hydrocarbons find a wide application as high-energy hydrocarbonic propellants for volume-limited rocket systems [1], as well as in pharmacology for obtaining modern antiviral pharmaceutical preparations; besides they are used in the creation of devices accumulating radiation energy of the Sun to transform it into thermal energy [2].

The classical approach to the synthesis of SPH *via* a consecutive cycle-by-cycle building is acceptable only for laboratory purposes and in solving structural problems due to a multi-stage nature of the process. The inefficiency of traditional methods is demonstrated well by the examples of synthesizing such high-strained hydrocarbons as prismane, cubane and, especially, dodecahedrane which have been obtained resulting from 40-stage process.

A prominent place in the synthesis of strained molecules of polycyclic hydrocarbons is by the right occupied by the method of metal complex catalysis. One could say with no exag-

geration that the complexes of transition metals are unique with respect to their efficiency in constructing small rings, since the former allow researchers to perform the synthesis of strained polycyclic and skeletal compounds at one stage using simple and accessible monomers. The reason of such a high efficiency is caused by the nature of metal complex catalytic action. The role of the central metal atom in a catalytic reaction is mainly determined by gathering reactant particles into the coordination sphere as well as by decreasing the energy barrier for the reaction to occur. In the case under consideration one can observe a considerable increase in the rate of a complicated reaction from the standpoint of entropy. Such a reaction is referred to as a “matrix reaction” and frequently results in the formation of two or more C–C bonds, *i.e.* in the cyclization (cycloaddition).

It should be noted that the complexes of transition metals use to catalyze $[2\pi + 2\pi]$, $[2\pi + 3\pi]$, $[4\pi + 24\pi]$ cycloaddition of olefins, dienes and acetylenes, so-called thermally forbidden pericyclic reactions. In the presence of metal complex catalysts all the types of cycloaddition proceed not as a coordinated process, but through a multistage mechanism, however all of them are completed by the formation of three-, four- and five-membered cycles.

At the same time, the successful synthesis of SPH could be carried out only basing on monomers those have a specific structure. Cycloaddition with the formation of small rings proceeds in the most ready manner for the monomers of unusual structure such as norbornene (NB), norbornadiene (NBD), cyclopropene, methylenecyclopropane and their derivatives, *i. e.* for such a series of compounds where the double bond is a part of the strained system. There is a plane deformation taking place in these molecules caused by the reduction of $C-C=C$ angle known as γ -straining. As a consequence, such molecules demonstrate a high reactivity in the reactions of cyclization where the straining in the transition state is considerably decreased (so, for cyclopropene the decrease amounts to 26 kcal/mol) [3]. The tendency of σ -strained monomers to the reactions of cyclization is most brightly exhibited in their transformations under the action of metal complex catalysts, in particular, in the processes of homocyclooligomerization. Alongside with this fact the tendency to cyclization inherent in γ -strained monomers is evident also in their joint transformations with linear unsaturated compounds (olefins, acetylenes, 1,2- and 1,3-dienes).

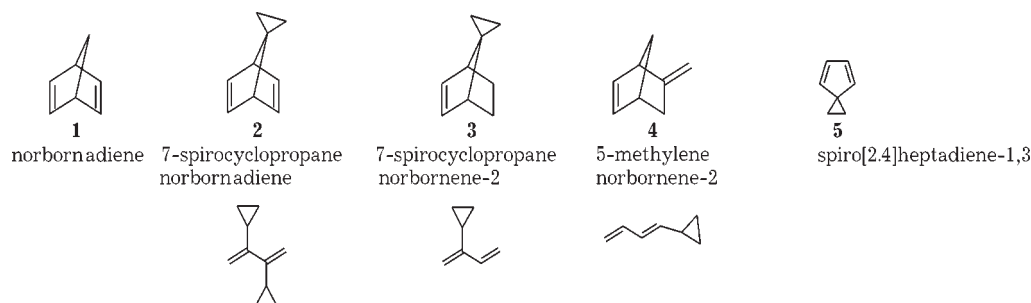
In connection with the presented above, within the framework of the program "Hydrocarbons" at the initial stage the collectives of the Laboratory of Catalytic Synthesis of the Institute of Organic Chemistry, USC of the RAS (Ufa), and of the Laboratory of Carbenes and Other Unstable Molecules of the Zelinsky Institute of Organic Chemistry, RAS (Moscow), have developed the methods for obtaining a whole family of monomers necessary for accomplishing of set tasks (Scheme 1).

Special hopes were pinned on NBD monomers, which resulted in the creation of a safe ("acetylene-free") technological method for two-stage obtaining NBD from chlorovinyl and dicyclopentadiene (cyclopentadiene) mastered in the industry soon [4].

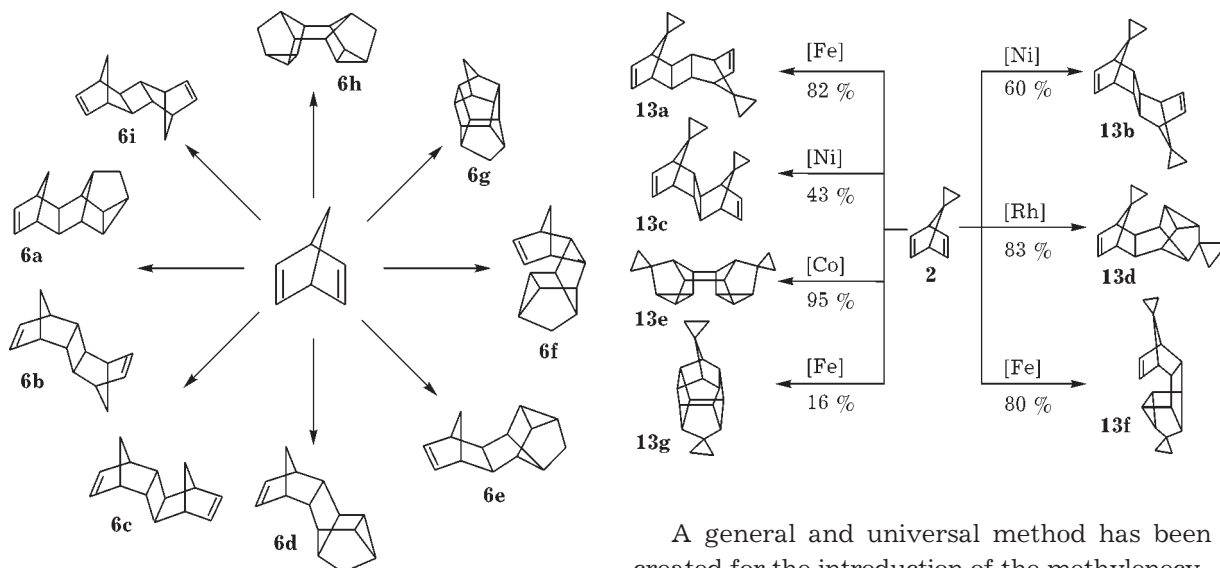
The presence of the mentioned family of initial monomers has allowed the research group consisting of two laboratories to realize one of the largest in the world programs for the development of new promising methods for the synthesis of high-strained polycyclic hydrocarbons built of three-, four- and five-membered rings. A whole series of novel transformations was postulated and carried out based on $[2\pi + 2\pi]$ -, $[2\pi + 3\pi]$ -, $[2\pi + 2\pi + 2\pi]$ -, $[4\pi + 2\pi + 2\pi]$ -, $[4\pi + 4\pi]$ cycloaddition reactions of NBD and its derivatives, 1,3-dienes, acetylenes and alkenes, which has allowed the researchers to develop new reactions and original methods for one-stage synthesis of three-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-, undeca- and dodecacyclic hydrocarbons non-described earlier or difficult-to-obtain [5, 6].

As the result of the studies performed we proposed highly active and selective Fe-, Co-, Ni- and Rh-containing catalysts for NBD homocyclodimerization allowing one to selectively obtain all the known stereoisomeric NBD dimers (**6a-i**) being both in an individual form, and as the mixtures of isomers with a preset structure (Scheme 2). The latter has is of important value for the creation of composite rocket propellants [5].

Furthermore, efficient Co-, Fe- and Pd-containing catalysts have been developed in order to carry out cross-cyclization of NBD and its valent isomer quadricyclane with stereoisomeric NBD dimers and trimers, which has allowed



Scheme 1.



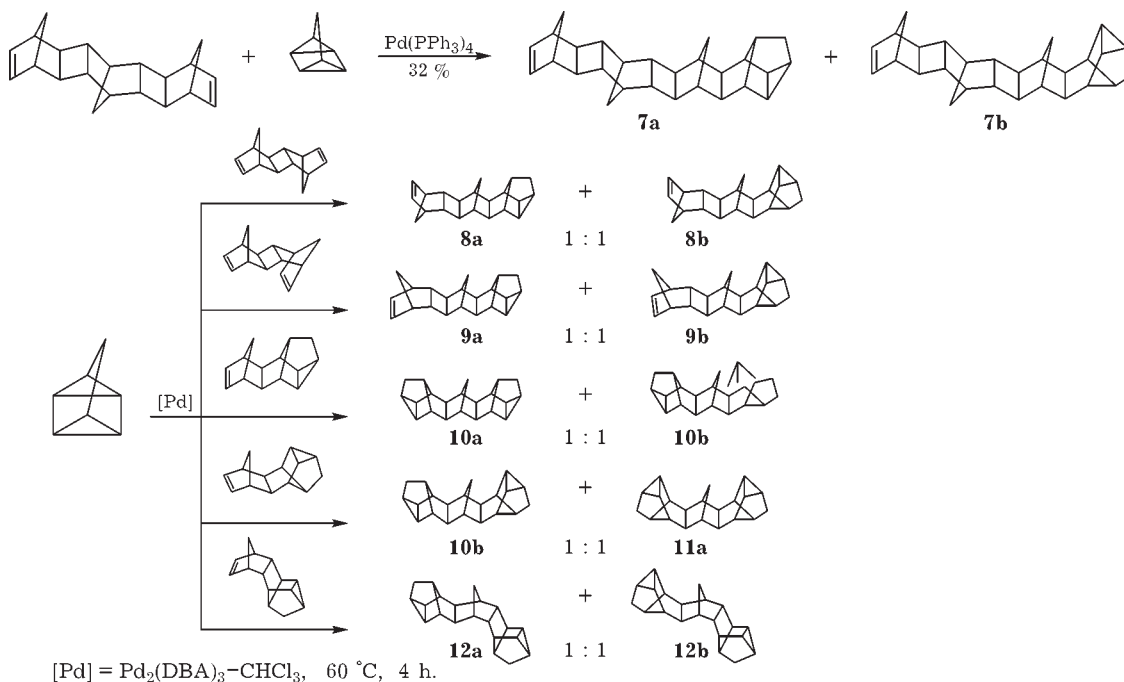
Scheme 2.

us to create methods for the synthesis of two NBD tetramers (**7a**, **7b**) as well as of nine novel stereoisomeric trimers (Scheme 3) [7–11].

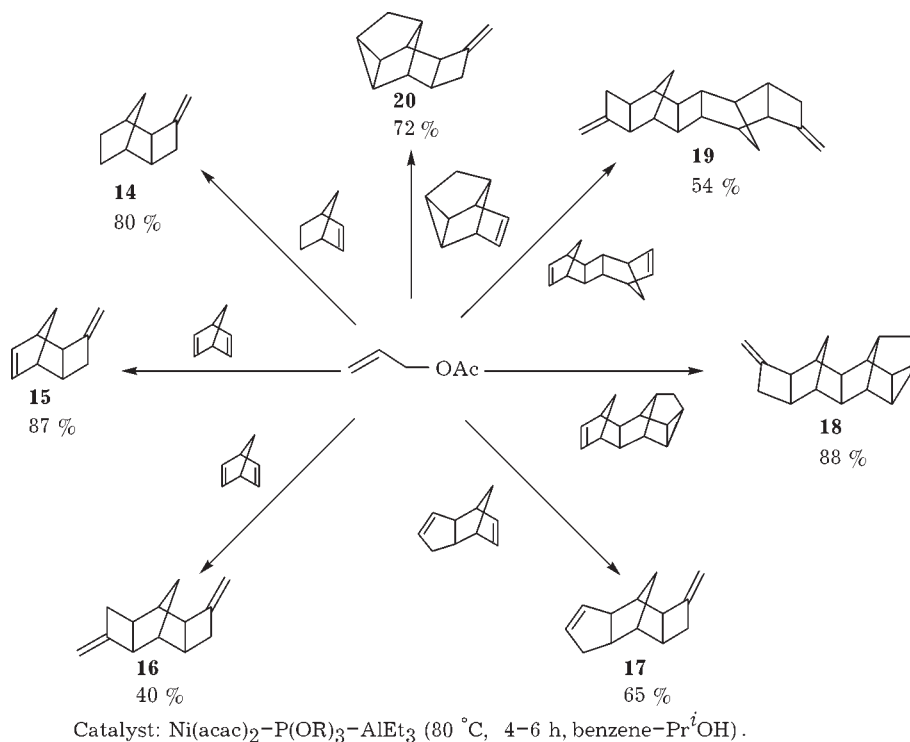
For the first time complex studies were performed concerning the basic laws of 7-spirocyclopropanenorbornadiene **2** cycloaddition under the action of Ni, Co, Fe and Rh complexes as well as highly active catalytic systems have been proposed those promote selective cyclodimerization of compound **2** resulting in the formation of hepta-, octa- and nonacyclic hydrocarbons (**13a–f**) with a high yield [11, 12]

A general and universal method has been created for the introduction of the methylenecyclobutane fragment into polycyclic olefins based on the interaction of NB, NBD and their derivatives with allylacetate under the action of complex Ni-containing catalysts (Scheme 4) [13].

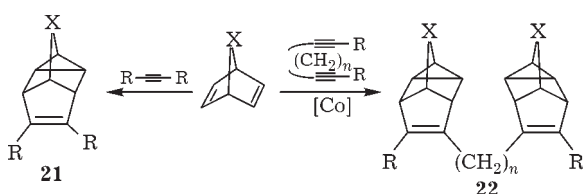
Catalytic cross-cyclization of NBD and its derivatives with acetylenes and allenes under the action of cobalt complexes has been realized according to $[4\pi + 4\pi]$ pattern assumed as a basis for a simple synthesis of hydrocarbons belonging to tetracyclo[4.3.0.0^{2,5}.0^{3,7}]nonane family. An extremely interesting modification of the mentioned reaction is presented by NBD and its derivatives cross-cyclization with diacet-



Scheme 3.



Scheme 4.

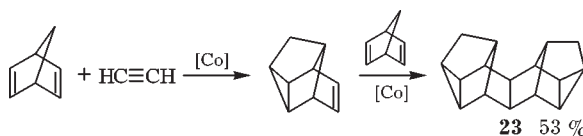


X = CH_2 , Δ ; R = H, CH_3 , $\text{C}_2\text{-C}_8$, Ph, Δ .
 $[\text{Co}] = \text{Co}(\text{acac})_2\text{-(Ph}_2\text{PCH}_2)_2\text{-AlEt}_2\text{Cl}$, 60 °C, 3 h, toluene.

Scheme 5.

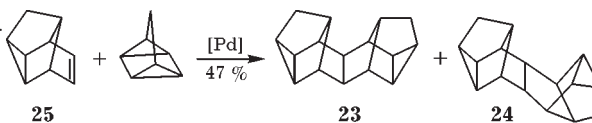
ylenes whose realization has offered a simple way to perform one-stage synthesis of bispolycycles **22** difficult-to-obtain earlier (Scheme 5) [14].

Due to the fact that we succeeded in performing the cascade cyclization of NBD with acetylene according to $[2\pi + 2\pi + 2\pi]$ pattern under the action of Co-containing catalysts, there appeared a possibility for realizing the synthesis of a novel class of high-strained hydrocarbons such as octacyclohexadecane **23**, built of eight small cycles [15]:



$[\text{Co}] = \text{Co}(\text{acac})_3\text{-(Ph}_2\text{PCH}_2)_2\text{-AlEt}_2\text{Cl}$, 60 °C, 2.5 h, toluene.

The same class of hydrocarbons with exo- (**23**) and endoconfiguration (**24**) has for the first time been synthesized through cross-cyclization of tetracyclo[4.3.0.0^{2.5}.0^{3.7}]nonene-8 **25** with quadricyclane under the action of palladium complexes [8].



$[\text{Pd}] = \text{Pd}_2(\text{DBA})_3\text{·CHCl}_3\text{-PPh}_3$, 60 °C, 2 h, toluene.

From the data presented one could see that as the result of the studies carried out within the framework of the research program, the methods have been developed for obtaining an extensive class of strained hydrocarbons, each of those could in sight become (for example, by analogy with adamantane) an ancestor of a whole family of compounds with useful properties. The results obtained offer a vast sphere of action for chemists engaged in synthesis. Among many transformation pathways of compounds obtained alongside with the functionalization, of particular interest is so-called stabilomeric synthesis, *i. e.* various skeletal rearrangements those could be induced using thermal, catalytic or photochemical action.

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