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# Catalytic cyclopropanation of hexa-1,3,5-triene with diazomethane as a simple synthesis of high-energy tercyclopropane

**Evgeny V. Shulishov, Olga A. Pantyukh, Leonid G. Menchikov and Yury V. Tomilov***

*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: tom@ioc.ac.ru*

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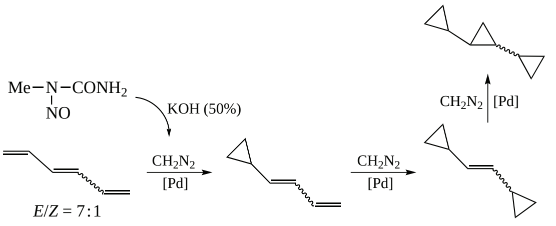
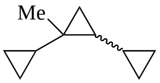
**A simple method for a preparing of tercyclopropane or 1,2-dicyclopropylethene by the catalytic cyclopropanation of hexa-1,3,5-triene with diazomethane has been developed. Thermochemical characteristics for tercyclopropane show that it may be a candidate to replace syntin as a propellant for spacecraft engines.**



*Keywords*: cyclopropane, tercyclopropane, diazomethane, liquid fuels, strained hydrocarbons, syntin.

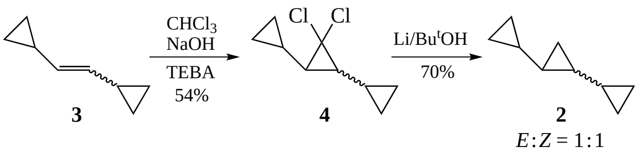
The cyclopropane fragment is an important structural element in organic chemistry, and in relation to hydrocarbons, due to the high strained energy of the three-carbon cycle, it can significantly increase the gravimetric energy intensity of hydrocarbon fuels.[1] Thus, among synthetic hydrocarbons that meet the tactical and technical requirements for rocket fuel for spacecraft, for a long time there was 1′-methyl-1,1′:2′,1″-tercyclopropane (syntin) **1**.[2–5] Despite the high efficiency of syntin as a rocket fuel, its production was based on scarce raw materials and consisted of many stages.[2] The industrial production of syntin was stopped in the 1990s, and since then, work has been underway to find its analogues, the synthesis of which should be simple and high-tech from available raw materials.



*E*/*Z*-**1**

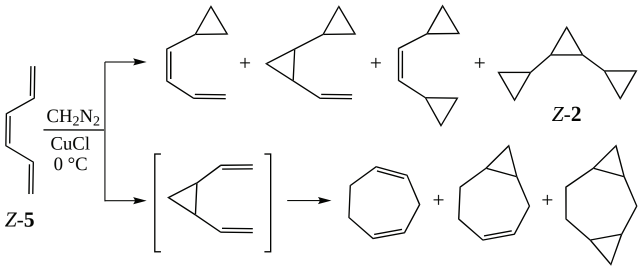
As a substitute for syntin, 1,2-dicyclopropylcyclopropane (tercyclopropane) **2**, whose molecule also contains three cyclopropane fragments and can exist as *E*- and *Z*-isomers, looks promising. Known synthesis of tercyclopropane is the addition of dichlorocarbene to 1,2-dicyclopropylethene **3** with subsequent reduction of the resulting 3′,3′-dichloro-1,1′:2′,1″-tercyclopropane **4** with lithium in *tert*-butanol (Scheme 1).[6] However, this two-stage scheme is based on poorly accessible 1,2-dicyclopropylethene **3** and is complicated technically.

A simpler and more efficient protocol for the synthesis of tercyclopropane can be a one-pot process for the exhaustive catalytic cyclopropanation of available hexa-1,3,5-triene **5**. The existing industrial production of triene **5** (85–90% *E*-isomer) in Russia is based on a single-step thermal catalytic cleavage of 6-methyl-3,6-dihydro-2*H*-pyran.[7] To date, a large number of other methods have been developed for the production of triene **5** both from traditional petrochemical products[8–10] and from plant materials.[11–13] The latter open up the prospect of creating methods for the industrial production of hexa-1,3,5-triene **5** from renewable resources.



**Scheme 1**

An attempt to cyclopropanate *Z*-hexa-1,3,5-triene *Z*-**5** with diazomethane was made almost 60 years ago.[14] However, that process employed explosive gaseous diazomethane and CuCl was used as a catalyst (Scheme 2). In that case, along with *Z*-**2** and the products of mono- and dicyclopropanation, other hydrocarbons were formed, resulting from the cyclization of *Z*-1,2-divinylcyclopropane and subsequent cyclopropanation of double bonds. As a result, the yield of the target product *Z*-**2** was 4% at a 3-fold molar excess of diazomethane and 48% at an 8-fold excess.



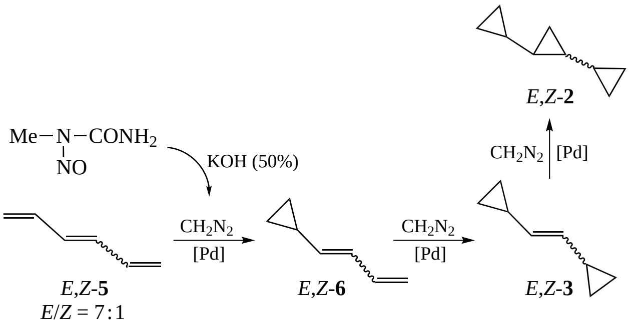
**Scheme 2**

From a practical point of view, the most convenient and economical process is catalytic cyclopropanation in which the generation of diazomethane in the course of alkaline decomposition of *N*-methyl-*N*-nitrosourea (MNU) proceeds simultaneously with its catalytic decomposition.[15] It is important to note that basically palladium compounds are efficient catalysts under these conditions. This method makes it possible to scale the cyclopropanation process and has prospects for pilot industrial application.[16,17]

In this work, we studied the cyclopropanation of hexa-1,3,5-triene **5** with diazomethane generated *in situ* using $(PhCN)_2PdCl_2$ and $Pd(acac)_2$ as catalysts. To assess the reactivity of double bonds, we used hexatriene **5** with a ratio of *E*- and *Z*-isomers of 7 : 1, obtained according to the described procedure.[7] The choice of [Pd] catalysts was based on their somewhat different efficiency in relation to the cyclopropanation of double bonds. Thus, the use of $Pd(OAc)_2$, $(PhCN)_2PdCl_2$ or olefin complexes of $PdCl_2$ as catalysts implies their initial reduction with diazomethane to the corresponding olefin complexes of $Pd^0$, which lose a nitrogen molecule in a reaction with diazomethane to give the corresponding cyclopropane *via* palladacyclobutane. The above catalysts work fairly well in the case of strained and terminal alkenes (hydrocarbons of norbornene series, styrene, 1-alkenes). With other unsaturated hydrocarbons, especially branched olefins, the target cyclopropanation nearly did not occur while the catalyst visually became the ‘palladium black’.[17,18]

The cyclopropanation of unsaturated hydrocarbons with diazomethane in the presence of palladium acetylacetonate, $Pd(acac)_2$, occurs somewhat differently. In this case, the reaction results in deeper conversion of the starting olefins, which is especially important for the cyclopropanation of inactive double bonds. It is assumed that, unlike the usual palladium compounds that are reduced with diazomethane to π-olefinic $Pd^0$ complexes, in the case of $Pd(acac)_2$ a more sophisticated palladium complex partially retaining the acetylacetone moiety serves as the active intermediate, which accounts for its greater stability in solution.[19]

Indeed, when $(PhCN)_2PdCl_2$ is used, as MNU is added to the reaction mixture (the amount of diazomethane generated during the decomposition of MNU is 75–78%), sequential cyclopropanation of the terminal double bonds of hexatriene **5** occurs with the predominant formation of 1-cyclopropylbutadiene **6** first, and then 1,2-dicyclopropylethene **3**, which after distillation can be obtained in 75 and 85% yields, respectively (Scheme 3, Table 1). This method can be considered as a convenient way to prepare these unsaturated synthons. Under these conditions, cyclopropanation of the internal double bond practically does not occur, and the reaction mixture itself turns black due to aggregation of the [Pd] catalyst.



**Scheme 3**

**Table 1** Catalytic cyclopropanation of a mixture of *E*- and *Z*-hexa-1,3,5-trienes **5**.[a]

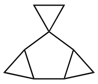
| Entry | Catalyst (0.2 mol%) | Ratio **5**/MNU[c] | Yields (%)[b] | | |
|---|---|---|---|---|---|
| | | | **6** (mono) | **3** (di) | **2** (tri) |
| 1 | $(PhCN)_2PdCl_2$ | 1 : 3 | **75** | 20 | – |
| 2 | $(PhCN)_2PdCl_2$ | 1 : 4.5 | 38 | 59 | 2 |
| 3 | $(PhCN)_2PdCl_2$ | 1 : 7 | 11 | **85** | 4 |
| 4 | $Pd(acac)_2$ | 1 : 3 | 68 | 22 | 6 |
| 5 | $Pd(acac)_2$ | 1 : 5 | 8 | 60 | 32 |
| 6 | $Pd(acac)_2$ | 1 : 7 | 1 | 9 | **90** |

[a] Ratio *E/Z* for starting hexatrienes and all compounds obtained was 7 : 1. [b] Conversion of hexatriene **5** is 96–100%. [c] MNU is *N*-methyl-*N*-nitrosourea (source of diazomethane), this sample contained about 12% water.

However, the use of $Pd(acac)_2$ as a catalyst and an excess of MNU leads to cyclopropanation of all double bonds. In this case, the conversion of the initial hexatriene reaches 100% and tercyclopropane **2** is obtained with a yield of up to 90% after removal of a small part of dicyclopropylethylene **3** by careful distillation (Table 1, entry 6). The ratio of *E*- and *Z*-isomers in all products **2**, **3** and **6** remained the same as in the starting hexatriene **5**.

It should be specially noted that the cyclopropanation of hexatriene **5** with diazomethane in the presence of palladium compounds is not complicated by any side transformations of starting triene or hydrocarbons **2**, **3**, **6**. The use of excess diazomethane is only necessary for compensating the side decomposition reactions of the latter to ethylene and cyclopropane, which are easily removed from the reaction mixture with the evolving nitrogen. For this reason, achieving a complete conversion of olefins to tercyclopropane seems to be unfavorable due to the unreasonably large use of MNU.

Further, we have determined herein the main thermochemical characteristics of tercyclopropane. Tercyclopropane **2** that we obtained has both a higher heat of combustion ($Q_{net}$ = 44150 kJ kg$^{-1}$) and higher density (0.863 g ml$^{-1}$) than syntin **1** ($Q_{net}$ = 44090 kJ kg$^{-1}$ and 0.850 g ml$^{-1}$, respectively[3,20,21]). Thus, tercyclopropane is superior to syntin both in the gravimetric net heat of combustion and volumetric net heat of combustion. Like syntin, tercyclopropane has a low freezing point (up to –75 °C). To estimate the prospects of certain hydrocarbons as fuels, calculation methods are usually employed. The specific impulse ($I_{sp}$) that is an important parameter determining the energy efficiency of fuel combustion was estimated using a method reported previously.[22] The results of calculating the thermochemical parameters and values of specific impulses (per unit mass) that we performed for syntin **1**, tercyclopropane **2**, as well as previously studied by us spiro[cyclopropane-1,5′-tricyclo[4.1.0.0$^{2,4}$]heptane] **7**, which also contains three cyclopropane rings,[19,23] are given in Table 2. The values of the heats of combustion and $I_{sp}$ were predicted for the complete combustion of hydrocarbon for a two-component system with $O_2$ as an oxidizer.[22]



*E*/*Z*-**7**

In conclusion, the use of available starting compounds and the simplicity of the suggested tercyclopropane synthesis, as well as its low freezing point and improved density and energy content, make tercyclopropane **2** an attractive candidate for

**Table 2** Calculated enthalpies of formation ($\Delta H_f$), gravimetric heat of combustion ($Q_{wt}$), heat of combustion of fuel (combustible + oxidant) ($H_{spec}$), and specific impulses ($I_{sp}$) for syntin **1**, tercyclopropane **2** and hydrocarbon **7** in the gas phase according to the method.[22]

| Compound | Formula | MW | $\Delta H_f$[a] | $\Delta H_{comb}$/ kJ mol$^{-1}$ | $Q_{wt}$/ kJ kg$^{-1}$ | $H_{spec}$/ kJ kg$^{-1}$ | $I_{sp}$/s[b] |
|---|---|---|---|---|---|---|---|
| *E*-**1** | $C_{10}H_{16}$ | 136.24 | –390.383394 | 5380 | 39496 | 9210 | 347.2 |
| *Z*-**1** | $C_{10}H_{16}$ | 136.24 | –390.383411 | 5380 | 39495 | 9210 | 347.2 |
| *E*-**2** | $C_9H_{14}$ | 122.21 | –351.095855 | 4847 | 39661 | 9281 | 348.5 |
| *Z*-**2** | $C_9H_{14}$ | 122.21 | –351.093691 | 4852 | 39707 | 9292 | 348.7 |
| *E*-**7** | $C_9H_{12}$ | 120.20 | –349.911078 | 4706 | 39162 | 9335 | 349.5 |
| *Z*-**7** | $C_9H_{12}$ | 120.20 | –349.901860 | 4731 | 39364 | 9383 | 350.4 |

[a] In arbitrary units, from DFT/6-31G(d,p) quantum-chemical calculation. [b] $I_{sp}$ normalized to dicyclobutyl [$I_{sp}$(exp) = 344.5 s].

further studies as a promising replacement to syntin as a propellant for spacecraft engines.

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.06.023.

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