ISSN 0965-5441, Petroleum Chemistry, 2008, Vol. 48, No. 4, pp. 309–313. © Pleiades Publishing, Ltd., 2008.
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Synthesis of Energetic Compounds via the Metathesis Reaction of 4-Methylenespiro[2,3]hexane

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Received July 20, 2007

Abstract—Transformations of methylenespiro[2,3]hexane (MSH) on a heterogeneous rhenium–alumina metathesis (disproportionation) catalyst were studied. It was found that, owing to a significant difference in the stability of carbenic complexes of methylene and disubstituted carbenes, MSH undergoes isomerization to 4-methylspiro[2,3]hex-4-ene followed by their cometathesis yielding bis(spiro[2,3]hexylidene-4). The feasibility of selective cometathesis of MSH and dicyclobutylidene on the rhenium–alumina catalyst resulting in the formation of 4-cyclobutylidenespiro[2,3]hexane was shown.

DOI: 10.1134/S0965544108040099

The development of some kinds of rocketry demands new liquid propellants with a high specific impulse. 4-Methylenespiro[2,3]hexane (I), the product of the cyclopropanation of one double bond in dimethylenecyclobutane (allene dimer), is a promising semiproduct for the synthesis of energetic materials. The presence of cyclobutane and cyclopropane rings in the molecule of compound I ensures a high energy density of this olefin. Therefore, the products of both its metathesis and cometathesis with unsaturated compounds containing strained carbocycles are of great interest.

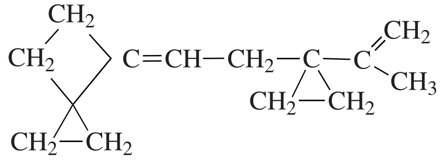
RESULTS AND DISCUSSION

A crude allene dimer is a mixture of two isomeric four-membered carbocycles, 1,2- and 1,3-dimethylenecyclobutane. As a consequence, the product of the cyclopropanation of the dimers is also a mixture of two isomers, namely, compound I and 5-methylenespiro[2,3]hexane. The ratio of isomers is 9–10 to 1, respectively.

Compound I with a purity of higher than 98 wt %, isolated via fractional distillation from the reaction mixture after the reduction of 2,2-dichloromethylenespiro[2,3]hexane contained metathesis-catalyst poisons as impurities. By gas chromatography–mass spectrometry and Fourier-transform IR spectroscopy, it was found that the distillate of compound I contains hydrocarbons with a molecular mass of 96 having a triple carbon–carbon bond, mainly in the α position. According to the IR data, the adsorption purification of I for the removal of these poisons by activated γ-aluminum oxide was ineffective. To establish the feasibility of metathesis for compound I, acetylenic compounds were removed from the olefin via a preparative procedure with the Ilosvay reagent [1].

Compound I did not undergo any transformations during the treatment with the reagent, which represents copper complexes. After purification, I had a 99 wt % purity. Being cleaned of acetylenic hydrocarbons, compound I reacted fairly well in the presence of a heterogeneous rhenium–alumina catalyst promoted with $PbEt_4$ or $SnBu_4$. In accordance with the traditional metathesis scheme, ethylene and bis(spiro[2,3]hexylidene-4) (II) had to be formed as the reaction products.

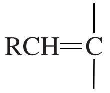
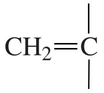
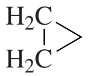
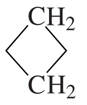
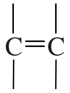
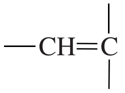
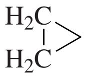
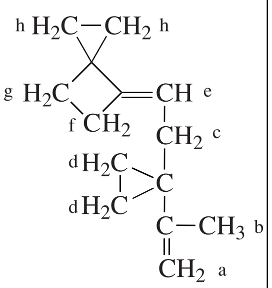
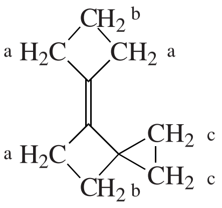
However, according to the gas chromatography–mass spectrometry data, the molecular masses of the heavy products of the transformation of I were 188, not 160 as it must be in the case of compound II. For identification, one of the products was isolated by preparative chromatography with a purity of 97 wt %. On the basis of IR, ^{1}H NMR, and mass spectral data (table), the isolated compound was identified as diene (III):



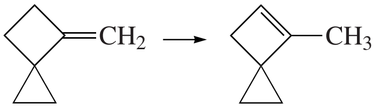
(III)

Other heavy products of the transformation of compound I are its isomers that differ in the position of cyclopropane rings. It is easy to see a certain resemblance of structures of this hydrocarbon and the previ-

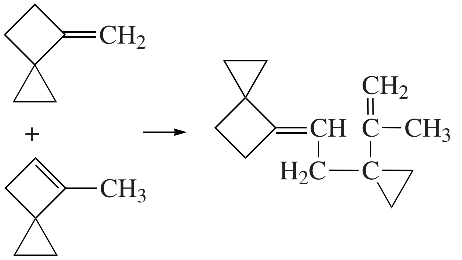
Physicochemical and spectral characteristics of compound **III** and diene **IX**

Structural formula	bp, °C/mmHg	n_d^{20}	d_4^{20}, g/cm^3	Spectra									
				^{1}H NMR, ppm	IR, cm^{-1}								Mass spectrum
					Structure fragment								
								$-CH_3$	 and CH_3			$CH_2{=}C$ and 	
	–	1.4984	–	0.35.0.46 (4H,b) 0.70.0.98 (4H,d) 1.60(3H,h) 1.65–2.10 (4H,c + g) 2.30–2.80 (2H,f) 4.70(2H,a) 4.65–5.05 (1H,e)	860	890	1015	1375	1425 1440	1645	1695	3008 3080	188/M$^+$3/,173(30) 159(36),145(24) 131(36),117(31) 107(96),105(50) 91(100),79(90) 65(26),53(36) 41(52)
	67/13	1.4991	0.9056	0.55,0.79 (4H, c) 2.05(4H,a) 2.46(6H,b)	–	–	1007	–	1429	–	–	3082	134/M$^+$47/119(32) 105(42),91(100) 79(33),65(15) 51(22),39(25) 27(12)

ously described 2-methyl-5-cyclobutylidenepentene-1 [2], one of the products of 1-methylcyclobutene cometathesis with methylenecyclobutane (IV), a structural analog of I. This similarity suggests that diene III is formed according to the following schemes:



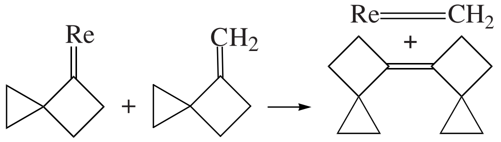
(1)



(2)

However, the mechanism of the formation of 4-methylspiro[2,3]hexane remains unclear. It is likely that this compound is formed via a route similar to the isomerization of IV into 1-methylcyclobutane on γ-Al_2O_3. But it may also be assumed that the isomerization occurs in the coordination sphere of the rhenium ion, which is the active center of metathesis.

The question of why diene III is formed instead of compound II is of considerable theoretical and practical interest. In terms of the carbene mechanism of metathesis, the transformation of I to II requires the transition from one carbene complex (V) to another carbene complex (VI) in accordance with scheme (3):

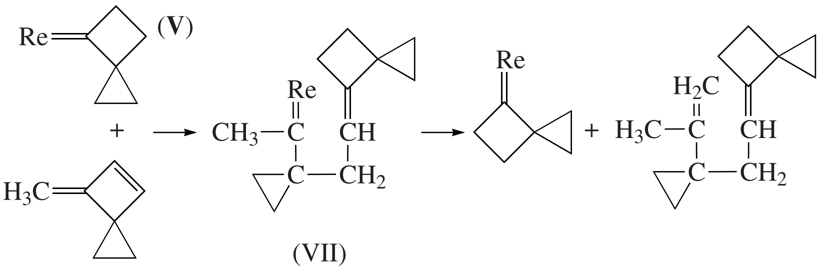


(V)

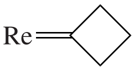
(VI)

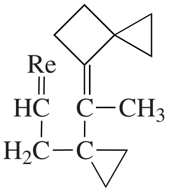
(3)

However, such a transition seems to be difficult because of the substantial difference in the stability of complexes V and VI. According to published data [3, 4], the carbene complex of methylene is one of the least stable complexes. In contrast, complex V must be considerably more stable, since it is a complex of a secondary carbene [3] and contains a three-membered ring capable of conjugation. At the same time, cometathesis reaction (2) shown above includes the transition of V to a structurally close complex of 1,1-disubstituted carbene (VII), which also has a three-membered ring capable of conjugation:



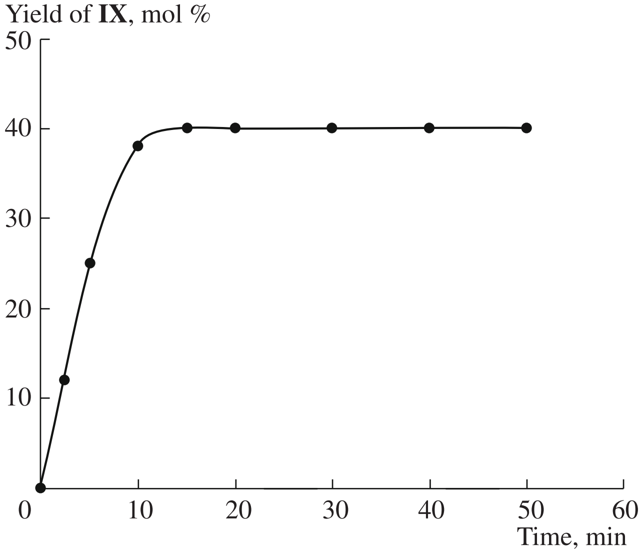
(4)

Note that this reaction differs from the cometathesis of IV with 1-methylcyclobutene; in the latter case, two variants of coordination of 1-methylcyclobutene to the carbene complex  were realized and two isomeric cometathesis products, 5-cyclobutylidenehexene-1 and 5-cyclobutylidene-2-methylpentene-1, were formed [2]. In our case, the single variant of the coordination depicted in scheme (4) was realized. The cause of this fact can be both steric hindrance to the formation of the alternative complex and a lower stability of the monosubstituted carbene (**VIII**) formed from this complex at the next stage.



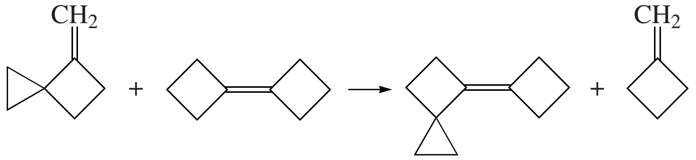
(VIII)

These facts suggest that the low reactivity of I in the metathesis is due to a high-energy barrier to the transformation of highly stable, relatively unreactive carbene complex V into the less stable complex VI. The reaction proceeds via another, energetically more favorable route involving the isomerization of I followed by the formation of carbene complex VII, which seems to be close in energy to complex V.



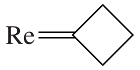
Kinetic curve for the formation of compound IX.

These speculations are confirmed by the effective cometathesis of compound I with dicyclobutylidene according to scheme (5):



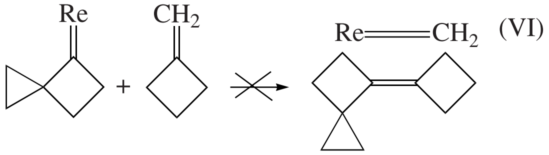
(5)

(IX)

In this case, the reaction requires the conversion of complex V to the structurally similar complex  and there is no need of the involvement of energy-rich methylene carbene. The cometathesis was conducted in the liquid phase at 35°C in the presence of the $PbEt_4$- or $SnBu_4$-promoted rhenium–alumina catalyst. The selectivity of the transformation of I into IX was about 90%. The kinetic curve of the process depicted in the figure indicates that, although the reaction initially proceeds at a high rate, the composition of the reaction mixture stops changing after approximately 20 min. This invariance can be explained by the thermodynamic constraints on the process.

4-Cyclobutylidenespiro[2,3]hexane (IX), the product of the cometathesis of compound I with dicyclobutylidene, was isolated by vacuum rectification to have a purity of 97 wt %. The structure of the product was confirmed by IR, ^{1}H NMR, and mass spectral data (table).

We failed to synthesize compound IX via the alternative cometathesis of I and IV according to scheme (6). It is likely that the failure is due to the fact that methylene complex VI should be produced at one of the reaction steps in this case:



(VI)

(6)

(V) (IV) (IX)

The same transformations of methylenespiro[2,3]hexane were observed under the conditions of its cometathesis with IV as those in the absence of IV, i.e., the isomerization of I to 4-methylenespiro[2,3]hex-4-ene and their metathesis.

EXPERIMENTAL

Analytical Methods

The gas-chromatographic/mass-spectrometric analysis of hydrocarbon mixtures and individual compounds was carried out with an LKB-2091 instrument (ion-source and molecular-separator temperatures of 250°C, an ionization energy of 70 eV, an emission current of 50 μA) on a 70000 × 0.25-mm capillary column coated with Apiezon L, as well as with a Kratos instrument on a 2000 × 3-mm column packed with 3% SE-30-coated Chromaton). The proton NMR spectra were recorded on a JEOL (100 MHz) instrument. The IR spectra were recorded with a Specord spectrophotometer in a 5% CCl_4 solution, as well as in the solvent-free mode.

Transformations of Methylenespiro[2,3]hexane (I) on Promoted Rhenium–Alumina Catalysts

The rhenium–alumina catalyst was prepared according to the conventional procedure [2]. The reaction was carried out at 35°C in a thermostated batch reactor equipped with a stirrer. A catalyst (0.78 g) preliminary activated at 580°C in a flow of air for 1 h and in a flow of nitrogen for 1 h was placed into the reactor. After thermostating, the catalyst was promoted with 1.3 wt % tetraethyl lead. Then, 3.9 ml (3.1 g) of compound I cleaned of acetylenic compounds was added. The reaction was accompanied by heat evolution. After 2 h, according to GLC data (SE-30, $l = 3$ m), the reaction mixture had the following composition (wt %): unreacted I, 53.88; diene III and its isomers, 38.86; and unidentified hydrocarbons, about 7.26. The yield of diene III and its isomers calculated in terms of reactant I taken was 39.25 mol %, and the selectivity of the conversion of I into these products was 86.13 mol %. Product III was isolated by preparative chromatography with a purity of 97 wt % (a PEG 1000 column; $l = 3$ m; and column and evaporator temperatures of 200 and 200°C, respectively). The structure of III and its physicochemical and spectral characteristics are given in the table. A mixture of the isomers of III was isolated with a purity of 95 wt %. The IR, ^1H NMR, and mass spectral data for diene III are given in the table.

Transformation of a Mixture of I and IV on $PbEt_4$-Promoted Rhenium–Alumina Catalyst

The reaction was carried out at 35°C in a batch system composed of a thermostated reactor equipped with a stirrer and an arrangement for the withdrawal of the ethylene produced. The 10% Re_2O_7/Al_2O_3 catalyst activated at 580°C was loaded into the reactor and promoted with tetraethyl lead (1.3 wt %) after cooling. Then, a mixture of I and IV was added. The mixture had the following composition (wt %): compound I, 10.05; compound IV, 89.69 wt %; unidentified impurities, 0.26. During the reaction, which lasted 2 h, ethylene was released. According to GLC data, liquid products contained unreacted compounds IV and I, as well as dicyclobutylidene resulting from metathesis, product III, and its isomers. The yield of diene III and its isomers calculated on the basis of reactant I fed was 21.63 mol % and that calculated on the basis of reactant I converted was 78.16 mol %. The yield of dicyclobutylidene calculated on the basis of reactant IV fed was 17.37 mol %, and the selectivity for dicyclobutylidene was 78.92 mol %.

Synthesis of 4-Cyclobutylidenespiro[2,3]hexane

The 10% Re_2O_7/Al_2O_3 catalyst activated in a nitrogen flow at 580°C was placed into a reactor similar to the one described above. After cooling, the catalyst was promoted with tetraethyl lead (1.3 wt %). The reactor was thermostated at 35°C, and a mixture of I (14.73 wt %) with dicyclobutylidene (83.56 wt %) was added to the reactor. The reaction was run at a constant temperature of 35°C with stirring for 2 h. Neither gas emission nor heat evolution was observed. According to GLC data, the resultant mixture contained unreacted compound I, dicyclobutylidene; compounds IV and IX as cometathesis products; and unidentified hydrocarbon impurities. The yield of IX on a fed reactant I basis was 45.29 mol %, the selectivity of the transformation of I was 96 mol %. The yield of IX on the fed dicyclobutylidene basis was 100 mol %. The desired product 4-cyclobutylidenespiro[2,3]hexane was isolated to have a 97 wt % purity via vacuum rectification followed by preparative chromatography under the aforementioned conditions. Its physicochemical and spectral characteristics are given in the table. The kinetics of the cometathesis reaction of compound I with dicyclobutylidene is illustrated in the figure.

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