

First Example of One-Pot Synthesis of Hydrocarbon Macrorings

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Abstract—Cyclomagnesation of α,ω -diallenes by EtMgBr in the presence of chemically activated Mg and Cp₂TiCl₂ catalyst led to the formation of cyclic organomagnesium compounds whose hydrolysis provided gigantic hydrocarbon macrorings with 1,5-*cis*-disubstituted double bonds.

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Syntheses of macrocyclic compounds are commonly multistage processes, cyclization reactions occur with low yields, and as a rule the isolation of target compounds is hampered by the presence of side oligomeric products [1, 2].

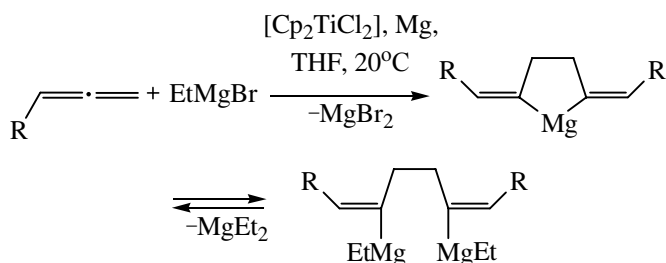
Among the important advances into the synthesis of macrorings should be cited studies [3–12] where the possibility was demonstrated to build up macrocyclic organometallic compounds by intermolecular cyclization of aromatic diacetylenes with the help of stoichiometric amounts of low-valence complexes of Co and Zr. Demetallation of the organometallic compounds obtained made it possible to synthesize the corresponding hydrocarbon macrorings containing aryl and 1,3-diene fragments in the chain [5–10].

The disadvantages of this method consist in the necessity to use diacetylenes of a specific structure, and in additional stage of preparing stoichiometric amounts of low-valence complexes of Co and Zr.

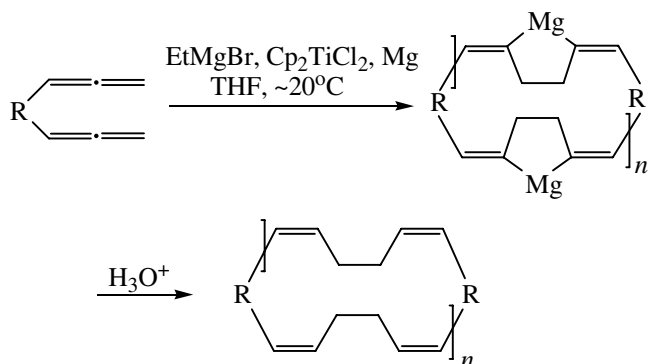
Aiming at development of a new general synthetic method for hydrocarbon macrorings promising for practical application we investigated for the first time the intermolecular cyclomagnesation α,ω -diallene with the use of EtMgBr catalyzed by titanium complexes.

In selection of the method for the synthesis of hydrocarbon macrorings we proceeded from our previous discovery of catalytic cyclomagnesation of monosubstituted

allenes by EtMgBr in the presence of Cp₂TiCl₂ catalyst giving 2,5-dialkylidenemagnesacyclopentanes [13].



We presumed that cyclomagnesation of the α,ω -diallenes by the Grignard reagents under the given conditions may lead to stereoselective intermolecular cyclomagnesation simultaneously of two or more molecules of the initial diallene providing macrocyclic organomagnesium compounds containing magnesacyclopentane



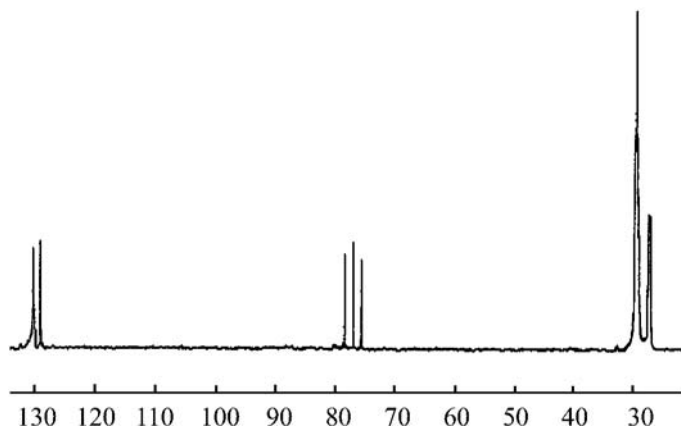


Fig. 1. ^{13}C NMR spectrum of compound **II**.

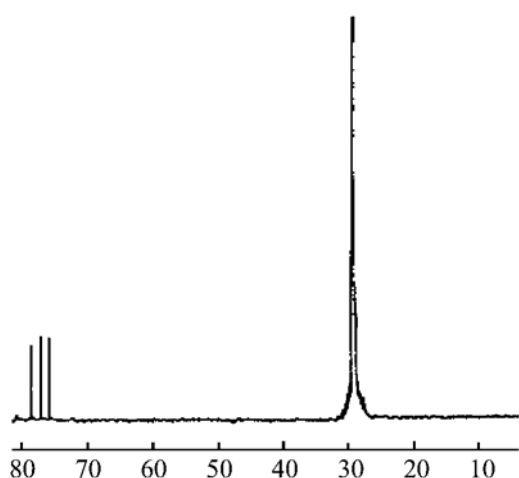


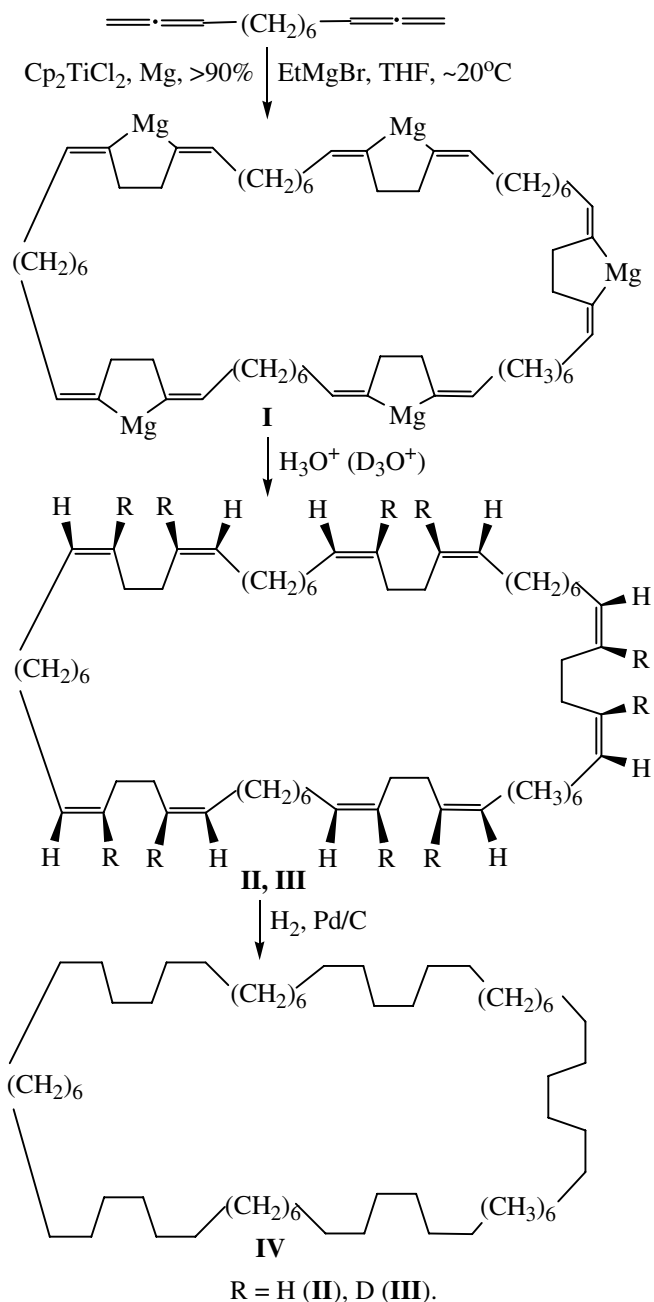
Fig. 2. ^{13}C NMR spectrum of saturated cyclic hydrocarbon **IV**.

fragments. On hydrolysis these products might give unsaturated hydrocarbon macrorings.

We chose for initial α,ω -di-allyne 1,2,10,11-dodecatetraene and studied the cyclomagnesation of the latter by EtMgBr (allene– EtMgBr ratio 1:1) in the presence of Cp_2TiCl_2 catalyst (10 mol%) and of chemically activated magnesium [14] used as halogen ions acceptor (THF, $\sim 20^\circ\text{C}$, 12 h).

Under these conditions we obtained from 1,2,10,11-dodecatetraene and EtMgBr macrocyclic compound **I**. Hydrolysis or quenching with deuterium oxide of compound **I** with the use of $\text{HCl}/\text{H}_2\text{O}$ or $\text{DCI}/\text{D}_2\text{O}$ resulted in macrorings **II** and **III** containing *Z*-double bonds. The hydrogenation of unsaturated macroring **II** with molecular hydrogen (5% Pd/C) provided cyclic saturated hydrocarbon **IV**.

^{13}C NMR spectrum of compound **II** contains upfield signals at δ 27.18 and 27.34 ppm corresponding to allyl



carbon atoms with the *cis*-configuration of the double bond, and strong peaks at 29.65 ppm belong to the methylene carbon atoms. Two downfield signals of olefin carbons appear at 129.19 and 130.30 ppm (Fig. 1). In the spectrum of partially deuterated macroring **III** obtained by quenching the organometallic macroring **I** with $\text{DCI}/\text{D}_2\text{O}$ the signals of atoms $\text{C}^{3,4}$ linked to deuterium α -isotope suffered upfield shifts ($\Delta\delta \sim 0.3$ ppm) are observed compared with the analogous signals of these carbons in the spectrum of compound **II** [15]. The lack in the NMR spectra of compound **II** of signals from

terminal double bonds or alkyl groups indicates its cyclic structure. ^{13}C NMR spectrum of compound **IV** resulting from the hydrogenation of unsaturated macro-ring **II** contains a single peak at 29.56 ppm (Fig. 2) corresponding to methylene carbon atoms; this fact also confirms the cyclic structure of compound **IV**.

Molecular weight of saturated hydrocarbon **IV** is 840 (as determined by mass spectrometry of positive ionization) [16], 836 ± 8 (by Rast method) [17]. The mass spectrum MALDI TOF of unsaturated macroring **II** contained the molecular ion peak of m/z 820. It means that polycyclic compound **I** initially formed by catalytic cyclomagnesation of 1,2,10,11-dodecatetraene gave on hydrolysis macrocyclic unsaturated hydrocarbon $\text{C}_{60}\text{H}_{100}$ (**II**) built of five molecules of the initial α,ω -diallene.

We did not succeed in growing a single crystal of macrocyclic compound **II** and thus we were not able to perform its X-ray diffraction study. The principal conformations of macromolecule **II** were simulated on a semiempirical level (AM1, Hyperchem 6.0, 2000). The calculations were carried out with respect to heat of formation and geometrical characteristics of various conformations, for the NMR spectra of these compounds did not give sufficient information on the prevailing conformations. It was shown that macroring **II** under study existed in a *twisted* conformation (Fig. 3). The most energetically favorable (~ 1.4 kcal per each fragment $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-$) is the conformer with the *trans*-located *Z*-double bonds. The observed intramolecular twisting of the unsaturated ring favors the approach of olefin bonds within the molecule (~ 3.2 Å) making possible their interaction. Presumably this is the reason why the unsaturated macroring **II** isolated from solution within several days becomes insoluble in common solvents, apparently due to the formation of a cross-linked polycyclic substance.

The data obtained permit a conclusion that the formation of macroring **I** containing five 2,5-dialkylidene-magnesyacyclopentane fragments occurs by intermolecular cyclomagnesation of α,ω -diallenes effected by RMgX in the presence of "titanocene" generated from Cp_2TiCl_2 [18].

Now we carry on active studies for extending the application field of this method to the synthesis of gigantic organomagnesium and hydrocarbon macrorings from α,ω -diallenes of diverse structures and to investigation of new classes of organomagnesium, hydrocarbon, and heteromacrocycles.

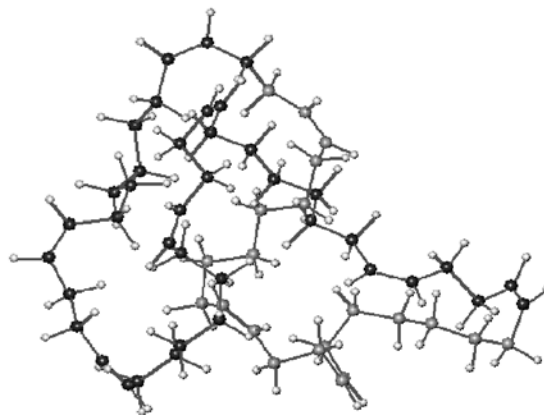


Fig. 3. Conformation of macroring **II** according to optimization using calculation method AM1.

EXPERIMENTAL

IR spectra were recorded on a spectrometer Specord 75IR (from films). ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-300 [300.13 (^1H) and 75.46 (^{13}C) MHz] from solutions in CDCl_3 . Mass spectra of positive ionization were obtained on a modified mass spectrometer MI-1201 [16] and on MALDI Voyager-D STR TOF. All experiments were carried out in an atmosphere of dry argon. EtMgBr solution in THF was prepared by procedure [19]. THF directly before use was distilled from LiAlH_4 under argon. Commercial Cp_2TiCl_2 was used in the study. Initial 1,2,10,11-dodecatetraene was synthesized as in [20].

Cyclomagnesation of 1,2,10,11-dodecatetraene. To 0.288 g (12 mmol) of magnesium activated by EtBr under an argon atmosphere at $\sim 0^\circ\text{C}$ was added 40 mmol of EtMgBr (1.4 M solution in THF), 10 mmol of 1,2,10,11-dodecatetraene, and 0.259 g (1 mmol) of Cp_2TiCl_2 . The reaction mixture was warmed to room temperature ($20\text{--}21^\circ\text{C}$), and it was stirred for 12 h. Then the reaction mixture was treated with 10% HCl or 8% DCl in D_2O . The reaction product was extracted with ether or hexane, dried with MgSO_4 , passed through a thin bed of alumina, and the solvent was distilled off in a vacuum. Hydrolysis product **II** was hydrogenated by H_2 (Pd/C) [21].

1,5,13,17,25,29,37,41,49,53-Cyclohexacontadecaene ($\text{C}_{12}\text{H}_{20}$)₅ (II**).** Yield 80%. IR spectrum, cm^{-1} : 730, 920, 1350, 1460, 1635, 2840, 2920. ^1H NMR spectrum, δ , ppm: 1.05–1.45 m (CH_2), 1.80–2.20 m ($\text{CH}_2\text{CH}=\text{}$), 5.25–5.55 m ($\text{CH}=\text{CH}$). ^{13}C NMR spectrum, δ , ppm: 130.30, 129.19, 29.65, 27.34, 27.18. Mass spectrum, m/z (I_{rel} , %): 820 [M]⁺ (0.8). Found, %: C 87.52; H 11.89. $\text{C}_{60}\text{H}_{100}$. Calculated, %: C 87.73; H 12.27.

2,5,14,17,26,29,38,41,50,53-Decadeutero-1,5,13,17,25,29,37,41,49,53-cyclohexacontadecaene (III). Yield 78%. IR spectrum, cm^{-1} : 710, 920, 1360, 1460, 1620, 2160 (CD), 2850, 2920. ^1H NMR spectrum, δ , ppm: 1.12–1.43 m (CH_2), 1.82–2.21 m ($\text{CH}_2\text{CH}=\text{}$), 5.23–5.51 m ($\text{CD}=\text{CH}$). ^{13}C NMR spectrum, δ , ppm: 130.32, 29.63, 27.32, 27.12 (carbon signals from the atoms of the double bond linked to deuterium were not observed). Found, %: C 86.44; (H+D) 12.91. $\text{C}_{60}\text{H}_{90}\text{D}_{10}$. Calculated, %: C 86.68; H 10.91; D 2.41.

Cyclohexacontane (IV). Yield >95%. IR spectrum, cm^{-1} : 730, 970, 1265, 1315, 1340, 1455, 1460, 2850, 2920. ^1H NMR spectrum, δ , ppm: 1.21–1.46 m (CH_2). ^{13}C NMR spectrum, δ , ppm: 29.56. M (calc.) 840. M (measured by Rast method [17]) 836 ± 8 . Mass spectrum, m/z (I_{rel} , %): 840 [M] $^+$ (1). Found, %: C 85.45; H 14.12. $\text{C}_{60}\text{H}_{120}$. Calculated, %: C 85.63; H 14.37.

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REFERENCES

1. *Host Guest Complex Chemistry: Macrocycles: Synthesis, Structures, Applications*, Vogtle, F. and Weber, E., Eds., Berlin: Springer, 1985.
2. Dietrich, B., *Macrocyclic Chemistry Aspects of Organic and Inorganic Supramolecular Chemistry*. Weinheim: VCH, 1993.
3. Ohkubo, A., Aramaki, K., and Nishihara, H., *Chem. Lett.*, 1993, p. 271.
4. Tomita, I., Nishio, A., Igarashi, T., and Endo, T., *Polym. Bull.*, 1993, vol. 30, p. 179.
5. Mao, S.S.H. and Tilley, T.D., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 5365.
6. Mao, S.S.H. and Tilley, T.D., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 7031.
7. Liu, F.-Q., Harder, G., and Tilley, T.D., *J. Am. Chem. Soc.*, 1998, vol. 120, p. 3271.
8. Mao, S.S.H., Liu, F.-Q., and Tilley, T.D., *J. Am. Chem. Soc.*, 1998, vol. 120, p. 1193.
9. Nitschke, J.R. and Tilley, T.D., *J. Org. Chem.*, 1998, vol. 63, p. 3673.
10. Nitschke, J.R., Zqrcher, S., and Tilley, T.D., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 10345.
11. Nitschke, J.R. and Tilley, T.D., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 10183.
12. Nitschke, J.R. and Tilley, T.D., *J. Organometal. Chem.*,
13. Dzhemilev, U.M., D'yakonov, V.A., Khafizova, L.O., and Ibragimov, A.G., *Tetrahedron*, 2004, vol. 60, p. 1287.
14. Lai, Y.-H., *Synthesis*, 1981, p. 585.
15. Breitmaier, E. and Voelter, W., *^{13}C NMR Spectroscopy*, Weinheim: Verlag Chemie, 1974, p. 127.
16. Vasil'ev, Yu.V., Tuktarov, R.F., and Mazunov, V.A., *Rap. Commun. Mass Spectrom.*, 1997, vol. 11, p. 757.
17. Rast, K., *Ber.*, 1922, vol. 55, p. 1051.
18. Shur, V.B., Berkovich, E.G., and Vol'pin, M.E., *J. Organometal. Chem.*, 1982, 228, vol. 36.
19. Ioffe, S.T. and Nesmeyanov, A.M., *Metody elemento-organicheskoi khimii. Podgruppy magniya, berilliya, kal'tsiya, strontsiya, bariya* (Methods of Organoelemental Chemistry. Subgroup of Magnesium, Beryllium, Calcium, Strontium, Barium), Moscow: Izd. Akad. Nauk SSSR, 1963, 561 p.
20. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.
21. Nesmeyanov, A.M., Nikitina, G.V., Nogina, O.V., Brainina, E.M., Posynskii, A.A., Magomedov, G.K.-N., Ioganson, A.A., Anisimov, K.N., Kolobova, I.E., Valueva, Z.P., Vyazankin, I.S., Shchelokov, R.N., Kruglaya, O.A., and Bolotova, G.T., *Metody elementoorganicheskoi khimii. Podgruppy medi, skandiya, titana, vanadiya, khroma, margantsa. Lantanoidy i aktinoidy* (Methods of Organoelemental Chemistry. Subgroup of Copper, Scandium, Titanium, Vanadium, Chromium, Manganese), Moscow: Nauka, 1974, 472 p.