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Functionalization of Fullerene C_{60} with Organic Carbonates in the Presence of a Grignard Reagent and Ti(Oi-Pr)$_4$ †

Liliya Khuzina * and Artur Khuzin

Institute of Petrochemistry and Catalysis, Ufa Federal Research Center of the Russian Academy of Sciences, 141 Oktyabrya Prospect, 450075 Ufa, Russia; artur.khuzin@gmail.com
* Correspondence: khuzina.liliya@gmail.com

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Abstract: Fullerene C_{60} is by far the most studied of all allotropic modifications of carbon. Chemical modification of the double bond over the years has led to the emergence of a variety of fullerene derivatives. These derivatives have now found numerous applications in medicine, materials, supramolecular chemistry, and as efficient electron acceptors in organic photovoltaic devices. The main method for the functionalization of C_{60} fullerenes, which makes it possible to obtain its derivatives in a preparative volume, is the Bingel-Hirsch reaction. But this method makes it possible to obtain fullerocyclopropanes containing only carboxyl substituents at the bridging carbon atom. Therefore, in order to obtain new materials, we began to study the interaction with organic carbonates in combination with Grignard reagents in the presence of Ti-containing complex catalysts. We hope that replacing the olefin in the Kulinkovich reaction with a C_{60}-fullerene molecule will lead to new and hard-to-find functionalization products of the latter. Organic carbonates were chosen as the object of study due to the fact that they are used in industry as solvents for natural and synthetic resins, cellulose ethers, dispersants, blowing agents, emulsifiers, absorbents of hydrogen sulfide and carbon dioxide, starting materials for the industrial synthesis of fibers and plastics, as well as as well as plasticizers, pharmaceuticals and plant protection products.

Keywords: organic carbonates; Grignard reagent; C_{60} fullerene

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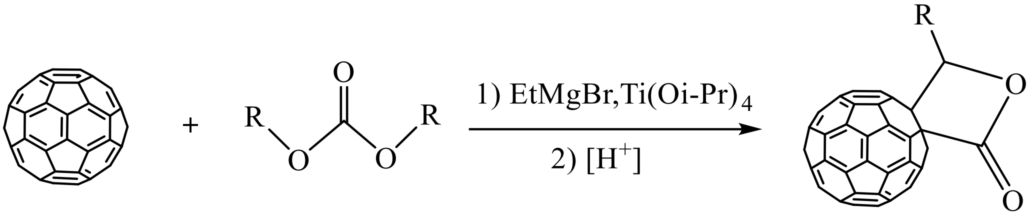
1. Introduction

Organic carbonates play an important role in modern organic synthesis [1,2]. They are used in the chemical industry as plasticizers, emulsifiers, solvents for natural and synthetic resins. In addition, carbonates are part of biologically active compounds in pharmaceuticals and agrochemicals [3,4]. Based on the above, in order to obtain new and promising materials for the chemical, pharmaceutical, agricultural industries and for photoelectronics, we decided to study the interaction of fullerene C_{60} with organic carbonates in combination with Grignard reagents in the presence of Ti-containing complex catalysts.

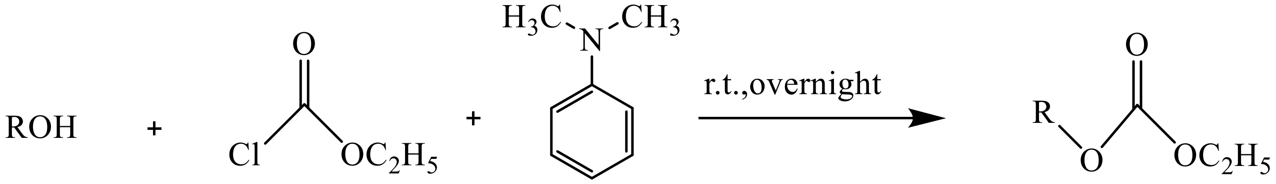
2. Results and Discussion

In the classical version of the Kulinovich reaction—hydroxy cyclopropanation of olefins with carboxylic acid esters is carried out using EtMgBr and Ti(Oi-Pr)$_4$ [5]. We assumed that replacing the olefin with a fullerene, the carboxylic acid ester with an organic carbonate will lead us to completely new fullerene derivatives.



Scheme 1. The main idea of our research.

In order to test our idea and select the most optimal conditions, it was necessary to obtain the simplest organic carbonates. The latter were obtained by the interaction of alcohols with ethyl chloroformate in the presence of triethylamine in a ratio of 1:1:1 (r.t., 3 h). Unfortunately, this method did not lead to a pure target product. According to [6], replacing triethylamine with N, N-Dimethylaniline (1.5 mol) leads to the required carbonates, which have a pleasant floral-fruity aroma.

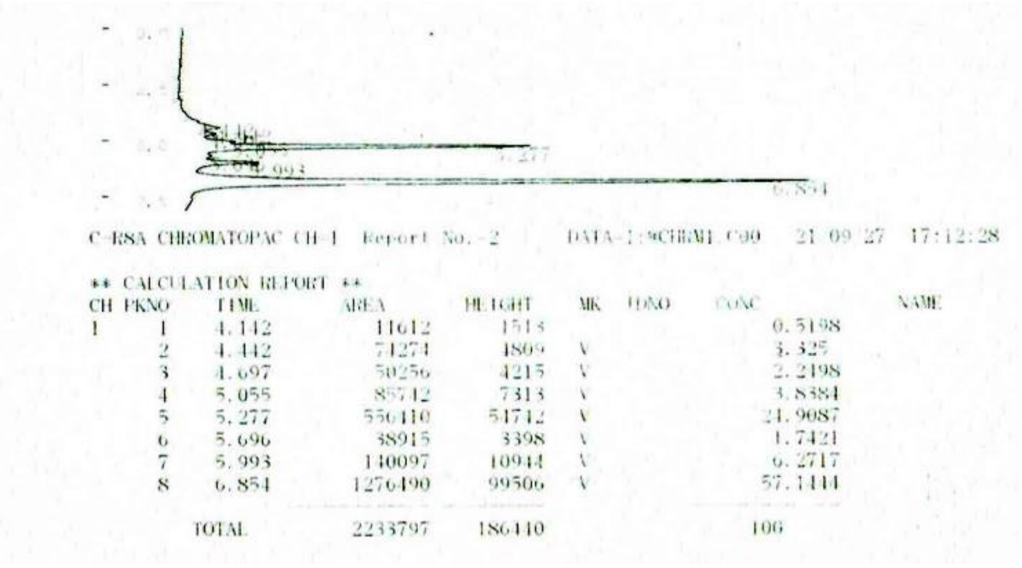


1: R=Bu; **2:** R=Hx; **3:** R=Bn

4: R=Bu; **5:** R=Hx; **6:** R=Bn

Scheme 2. Synthesis of carbonates.

Preliminary experiments have established that the interaction of C_{60}-fullerene can be realized only with an aryl-containing carbonate. Thus, ethyl phenyl carbonate interacts with fullerene C_{60} in the presence of Ti(Oi-Pr)$_4$ and EtMgBr at 80 °C with a reagent ratio of 5:1:15:15 for 1 h.



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C-R8A CHROMATOPAC CH=1  Report No.=2        DATA=1:@CHRM1.C00   21/09/27  17:12:28

** CALCULATION REPORT **
CH PKNO     TIME      AREA       HEIGHT    MK  IDNO   CONC              NAME
1    1      4.142       11612      7513                  0.5198
     2      4.442       74274      1809    V             3.325
     3      4.697       50256      4215    V             2.2498
     4      5.055       85742      7313    V             3.8384
     5      5.277      556410     51742    V            24.9087
     6      5.696       38915      3398    V             1.7421
     7      5.993      140097     10944    V             6.2717
     8      6.854     1276490     99506    V            57.1444

          TOTAL       2233797    186440                100
```

Figure 1. HPLC chromatogram of the reaction mixture.

The reaction progress was monitored by analytical HPLC. The peak at 5.277 min belongs to the fullerene derivative, and the peak at 6.854 to unreacted free fullerene.

Increasing the temperature, reaction time, and changing the reagent ratio leads to an increase in the intensity of the peaks at the 4th minute, which corresponds to polyaddition products.

Using semi-preparative HPLC, an individual adduct was isolated from the resulting reaction mass. One-dimensional (^1H and ^{13}C) experiments showed that under the conditions we selected, a product different from our idea is formed. At the moment, this derivative is being developed for two-dimensional (HHCOSY, HSQC, HMBC) NMR spectroscopy and mass spectrometry in order to reliably establish the structure of the fullerene derivative.

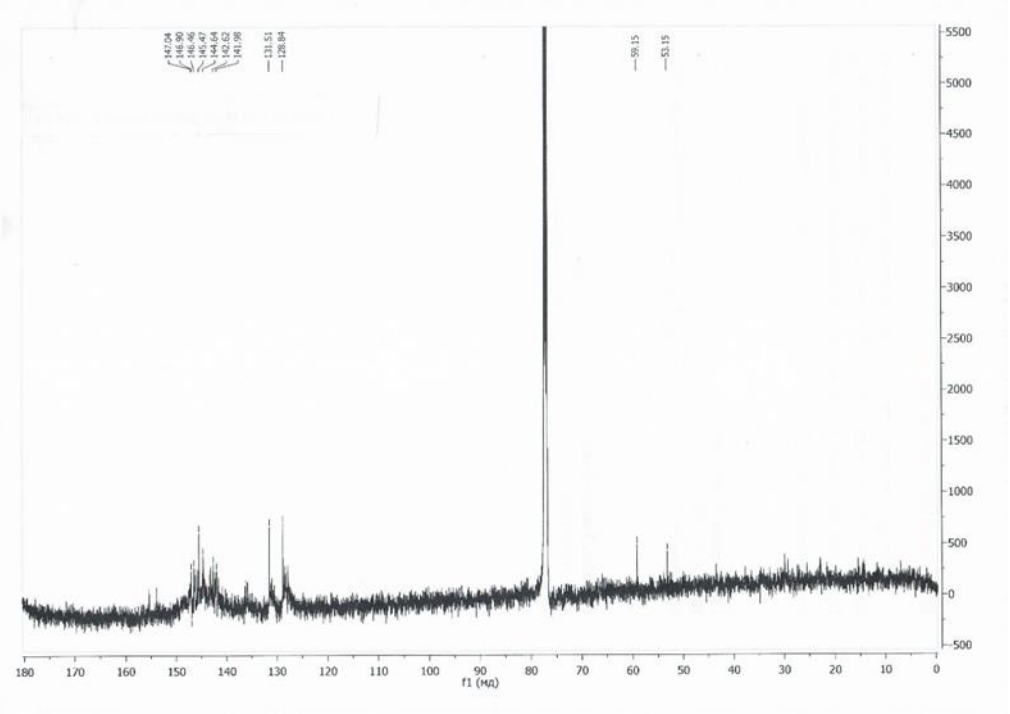

Figure 2. NMR spectrum of an individual fullerene derivative (125 MHz, $CDCl_3$).

In order to develop our idea, it is planned to study the influence of the nature of the alkyl and halogen substituents of the Grignard reagent RMgX on the yield of target adducts, the influence of hydrolysis conditions (RCOH, D_2O) on the quality of the target product and the use of a wider range of carbonates with different substituents.

3. Conclusions

Thus, preliminary experiments have established that the interaction of fullerene C_{60} under the conditions of the Kulinkovich reaction is possible only with aryl-containing organic carbonates.

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Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Parrish, J.P.; Salvatore, R.; Jung, K.W. Perspectives on Alkyl Carbonates in Organic Synthesis. *Tetrahedron* **2000**, *56*, 8207–8237.
2. Shaikh, A.-A.G.; Sivaram, S. Organic Carbonates. *Chem. Rev*. **1996**, *96*, 951–976.
3. Mohamed, N.; Paull, K.D.; Narayanan, V.L. Computer-Assisted Structure–Anticancer Activity Correlations of Carbamates and Thiocarbamates. *J. Pharm. Sci.* **1985**, *74*, 831–836.
4. Kole, H.K.; Akamatsu, M.; Ye, B.; Yan, X.J.; Barford, D.; Roller, P.P.; Burke, T.R. Protein-Tyrosine Phosphatase Inhibition by a Peptide Containing the Phosphotyrosyl Mimetic, L-O-Malonyltyrosine (L-OMT). *Biochem. Biophys. Res. Commun.* **1995**, *209*, 817–822.
5. Kulinkovich, O.G.; Meijere, A. n-Dicarbanionic Titanium Intermediates from Monocarbanionic Organometallics and Their Application in Organic Synthesis. *Chem. Rev*. **2000**, *100*, 2789–2834.
6. Holden, D.A. Synthesis and spreading behavior of some reactive derivatives of long-chain alcohols and carboxylic acids. *Can. J. Chem.* **1983**, *62*, 574–579.