

## Unusual reaction of 8-chloro-2-cyclohexyl-4-phenylbenzo[*e*]-1,2-oxaphosphinine-2-oxide with tetramethylenebis(magnesium bromide)

Dmitry A. Tatarinov,<sup>a,b</sup> Vladimir F. Mironov,<sup>\*a,b</sup> Elena N. Varaksina,<sup>a</sup> Dmitry B. Krivolapov,<sup>a</sup> Igor A. Litvinov,<sup>a</sup> Rashid Z. Musin,<sup>a</sup> Boris I. Buzykin<sup>a</sup> and Alexander I. Konovalov<sup>a,b</sup>

<sup>a</sup> A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 843 275 5322; e-mail: mironov@iopc.knc.ru

<sup>b</sup> A. M. Butlerov Chemical Institute, Kazan State University, 420008 Kazan, Russian Federation

DOI: 10.1016/j.mencom.2008.05.012

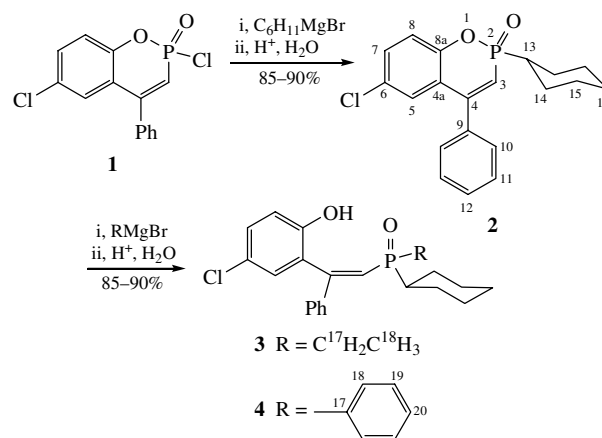
The reaction of 8-chloro-2-cyclohexyl-4-phenylbenzo[*e*]-1,2-oxaphosphinine-2-oxide with ethyl- and phenylmagnesium bromides and tetramethylenebis(magnesium bromide) is a versatile approach to the synthesis of unsymmetrical phosphine oxides. With the latter Grignard reagent, an unusual phosphorus–carbon cleavage also occurs to yield a pentacoordinate phosphorus derivative, 2,3,8,9-bis(4-chlorobenzo)-6-cyclohexyl-6,9-diphenyl-1,7-dioxo-6-phosphaspiro[5.5]deca-1,9-diene.

Achiral ( $R_3P=O$ ), prochiral ( $R_2R^1P=O$ ) and chiral ( $R^1R^2R^3P=O$ ) phosphine oxides are the main precursors in the syntheses of corresponding phosphines,<sup>1–11</sup> which are widely used as ligands in metal complex catalysts<sup>2,4,6,10,12</sup> and neutral extracting agents for rare-earth metals.<sup>13–17</sup> Phosphine oxides can also be used as ligands in reactions catalysed by palladium and molybdenum complexes.<sup>18–20</sup> The syntheses of phosphine oxides include reactions of organolithium and organomagnesium compounds with acyclic derivatives of tetracoordinate phosphorus containing alkoxy groups or chlorine atoms<sup>21–23</sup> or addition of hydrophosphoryl compounds to C=C bonds.<sup>24</sup> Reactions of organolithium and organomagnesium compounds with phosphorus derivatives containing both alkoxy groups and chlorine atoms are characterised by medium or low chemoselectivity. The use of Grignard reagents results in phosphine oxide mixtures, which are difficult to separate.

In this work, we attempted to obtain unsymmetrical phosphine oxides containing dissimilar substituents at the phosphorus atom, viz., six-membered phosphorus-containing heterocycles with one phosphorus–oxygen bond, such as 2,8-dichloro-4-phenylbenzo[*e*]-1,2-oxaphosphinine-2-oxide **1**. Compound **1** also contains an active phosphorus–chlorine bond and can be easily obtained by the reaction of phenylacetylene with 2,2,2-trichlorobenzol-1,3,2-dioxaphosphole.<sup>25</sup> Phosphinine **1** selectively reacts with cyclohexylmagnesium bromide to give only 8-chloro-2-cyclohexyl-4-phenylbenzo[*e*]-1,2-oxaphosphinine-2-oxide **2**, in a high yield. Note that introduction of the second cyclohexyl radical does not occur due to the sterical effect of this substituent in the Grignard reagent. The structure of compound **2** was confirmed by NMR spectroscopy and mass spectrometry.<sup>†</sup> Derivative **2**

containing a chiral phosphorus atom is capable of reacting with Grignard reagents obtained from non-branched alkyl halides or aryl halides; this reaction affords phosphine oxides **3**, **4** with three different substituents through the cleavage of the oxaphosphinine heterocycle (Scheme 1).<sup>†</sup>

The reaction of 8-chloro-2-cyclohexyl-4-phenylbenzo[*e*]-1,2-oxaphosphinine-2-oxide with tetramethylenebis(magnesium bromide) is unusual. The formation of diphosphine oxide derivative **5** is not the major pathway of the reaction (Scheme 2).<sup>‡</sup> The main pathway is the unexpected formation of spirophosphorane derivative **9** (its content is 47% in the reaction mixture after hydrolysis). We failed to find data on a similar behaviour of Grignard reagents toward phosphorus derivatives, though examples of sulfur–carbon bonds cleavage were reported.<sup>26</sup>



Scheme 1

Scheme 2 shows a possible pathway for the formation of this compound, which involves a reaction of phosphinine oxide **2** with an organomagnesium compound to yield organodimagnesium derivative **6** or its cyclic form **6a** (examples of similar organodimagnesium derivatives are known<sup>27</sup>). A similar reaction may be considered as the ligand replacement of the basic radical by more acidic one at a magnesium atom. This process should also give a molecule of 2-cyclohexyltetrahydrophosphole-2-oxide **7**, which has not been isolated. However, its presence follows from the chemical shift of the corresponding signal in the <sup>31</sup>P NMR spectrum ( $\delta_p$  78.2 ppm) of the reaction mixture, which agrees with the corresponding values for similar compounds, containing

<sup>†</sup> Melting points (uncorrected) were measured with a Boetius melting point apparatus. NMR spectra were recorded with Bruker Avance-600 (<sup>1</sup>H, 600 MHz; <sup>13</sup>C, 150.9 MHz), Bruker Avance-400 (<sup>1</sup>H, 400 MHz; <sup>13</sup>C, 100.6 MHz) and Bruker CXP-100 (<sup>31</sup>P, 36.48 MHz) spectrometers. The  $\delta_H$  and  $\delta_P$  values were determined relative to internal (HMDS) or external (H<sub>3</sub>PO<sub>4</sub>) standards. The IR spectrum was recorded with a Bruker Vector-22 instrument in Nujol. EI mass spectra were obtained with a TRACE MS Finnigan MAT instrument; the ionization energy was 70 eV and the ion source temperature was 200 °C. The samples were introduced into the ion source *via* a direct inlet system. The evaporating ampoule was heated from 35 to 150 °C at a rate of 35 K min<sup>-1</sup>. The mass spectrometric data were processed using the Xcalibur program.

For syntheses and characteristics of compounds **2–4** see Online Supplementary Materials.