

An unusual non-symmetrical nitrile ylide dimerization catalyzed by bis(diisopropylamino)carbene

Dmytro Poliakov, Alexey Rogalyov and Igor Shevchenko*

Institute of Bioorganic Chemistry and Petrochemistry, Murmanskaya Street 1, 02094 Kiev, Ukraine

Received 15 May 2007; revised 3 July 2007; accepted 12 July 2007

Available online 21 July 2007

Abstract—Carbene–nitrile ylide **2** undergoes an unusual non-symmetrical dimerization catalyzed by stable bis(diisopropylamino)-carbene.

© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

There are only a few examples of phosphorus ylides known in which the P=C ylidic bond is capable of dissociation with the formation of phosphanes and carbenes.^{1–3} Cleavage of the highly polarized ylidic bond can be considered as a self-reduction of the ylidic phosphonium centre. Recently, we found that ylide **1**, in which the negative charge on the ylidic carbon atom is delocalized onto the hexafluoroisopropylimino group, dissociates reversibly in organic solvents to give triphenylphosphine and carbene–nitrile ylide **2**.⁴ The equilibrium is strongly shifted to the ylidic form and the dissociation products cannot be detected in the reaction solution by NMR spectroscopy due to their low concentrations. However, compound **2** can be easily trapped by different reagents. For example, the dissociation of ylide **1** in the presence of cyclohexane or phenylisocyanate results in the formation of triphenylphosphine and the appropriate 1,3-addition products.⁴

In these reactions, compound **2** displays properties of the mesomeric nitrile ylidic form **2b**. This is in agreement with the other known examples in which this type of compound, generated by different methods, only took part in 1,3-addition reactions.⁵

There are only a few examples known where nitrile ylides behave as imine-substituted carbenes, all of which

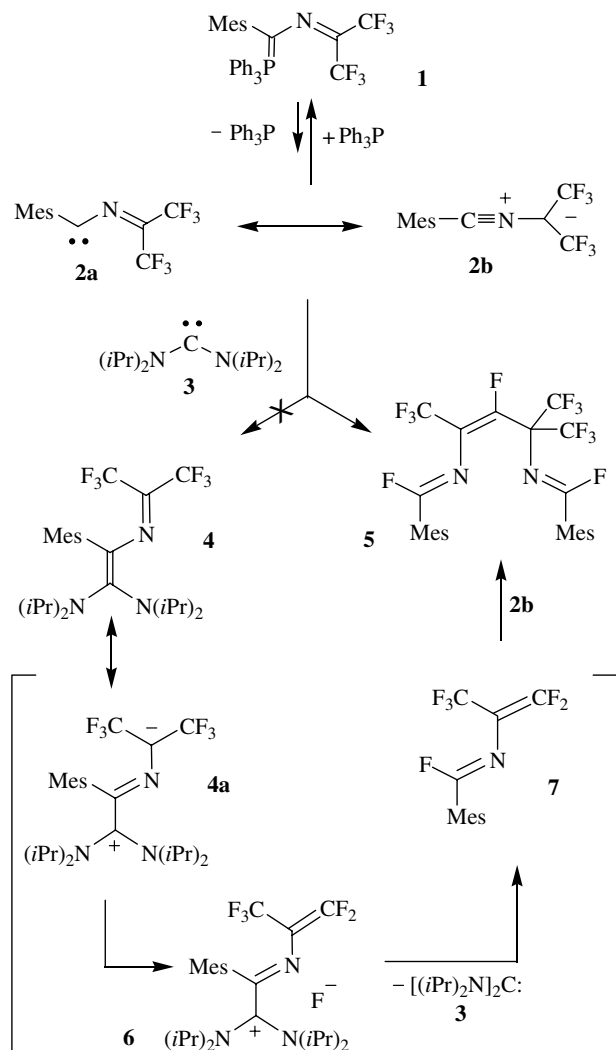
lead to dimerization.^{6,7} The dissociation of the ylidic bond of **1** and the recombination of products should also be considered in terms of the carbene-like reactivity of **2**. We reasoned that compound **2** would display carbene-like properties in reactions with other carbenes. For this purpose it was decided to conduct the decomposition of ylide **1** in the presence of stable bis(diisopropylamino)carbene **3**. We expected that the reaction between these two carbenes would give alkene **4**.

However, the actual result turned out to be rather unexpected. The reaction proceeded smoothly at 40 °C and in 30 min resulted in an almost quantitative formation of triphenylphosphine and non-symmetrical dimer **5**, which did not contain diisopropylamino groups (Scheme 1). Carbene **3** acted as a catalyst in this reaction and remained unchanged in the reaction mixture. Without catalytic quantities of **3** the starting ylide **1** was stable in solution and could be heated at 40 °C without any changes for several hours.

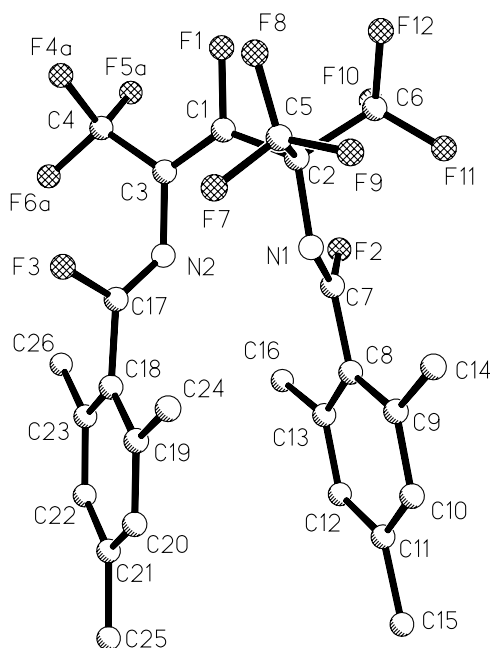
Compound **5** can be isolated from the reaction mixture by column chromatography in good yield as a colourless crystalline product. The structure of **5** was unambiguously established by X-ray analysis (Fig. 1). Formally this compound can be considered as a non-symmetrical dimer of compound **2**. The mechanism of the reaction is not quite clear. One can suppose that carbene **3** interacts with the decomposition product **2** but not with the starting ylide **1**. This is supported by the fact that the reaction time does not depend on the quantity of carbene **3** added and that the ³¹P NMR spectrum of the reaction mixture displays only signals of the starting ylide **1** and triphenylphosphine. The catalytic activity of carbene **3** is based on its ability to form new bonds combined with

Keywords: Carbenes; Dissociation; Homogeneous Catalysis; Nitrile ylides; Ylides.

* Corresponding author. Tel.: +380 44 5732589; fax: +380 44 5732552; e-mail: igorshvchenko@yahoo.com



Scheme 1.

Figure 1. Crystal structure of **5**.

high nucleophilicity leading to the formation of a stable formamidinium cation. It cannot be excluded that the expected compound **4** may participate in this reaction as an intermediate capable of undergoing elimination of F^- . This compound can be described by the mesomeric zwitterionic form **4a** containing a formal negative charge on the carbon atom between the CF_3 groups, which should facilitate elimination of the fluoride anion to form isomeric structure **6**. Probably compound **6** undergoes decomposition with expulsion of free carbene **3** and formation of the electrophilic hexafluorinated azadiene **7**, which nitrile ylide **2b** can attack. It is quite possible that **6** reacts with **2** first and then undergoes decomposition to give carbene **3** and product **5**. These two processes can also be concerted.

In crystalline form compound **5** is rather symmetrical as the N(2), C(3), C(1), C(2) and N(1) atoms are situated almost in the same plane (Fig. 1). The N(1) and N(2) atoms are slightly deviated from this plane. For example, the C(2)–C(1)–C(3)–N(2) and C(3)–C(1)–C(2)–N(1) dihedral angles are $-9.5(4)^\circ$ and $11.4(4)^\circ$, respectively. It is interesting that despite the possibility of rotation around the C1–C2 bond the two mesityl groups are situated very close and almost parallel to each other.

The two adjacent CF_3 groups are not symmetrical and occupy different environments in crystalline form because the C(7)–N(1) and C(17)–N(2) bonds are nearly perpendicular to the plane N(2), C(3), C(1), C(2), N(1). The corresponding dihedral angles C(1)–C(2)–N(1)–C(7) and C(1)–C(3)–N(2)–C(17) are $69.1(3)^\circ$ and $107.6(3)^\circ$, respectively. In solution, however, compound **5** has higher symmetry as both CF_3 groups display a common signal at $\delta = -71.34$ ppm in the ^{19}F NMR spectrum. This is probably accounted for by free rotation around the N(1)–C(2) and N(2)–C(3) bonds.

It is quite possible that the non-symmetrical dimerization of nitrile ylide **2** catalyzed by bis(diisopropylamino)carbene **3** is not a specific case but may have a more general character. The catalytic activity of stable nucleophilic carbenes and their use as ligands in organometallic and inorganic coordination chemistry has generated much interest in the last decade.^{8–11}

2. Experimental

Compound 5. Bis(diisopropylamino)carbene¹² (**3**; 4.4 mg, 0.0207 mmol) was added to a solution of ylide **1** (57.4 mg, 0.103 mmol) in benzene- d_6 (0.7 mL) at room temperature. The reaction solution was heated for 30 min at 40°C affording a dark coloured mixture. After evaporation of the solvent in vacuo the residue was extracted with hexane (2×1 mL); the extract was concentrated and purified by column chromatography ($R_f = 0.25$ – 0.3 , silica gel 60, hexane) to give **5** as colourless crystals (yield: 23.4 mg, 77%). Mp 111 – 112°C ; ^1H NMR (400 MHz, CDCl_3 , 20°C): δ 2.17 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 6.67 (s,

2H, C₆H₂), 6.72 (s, 2H, C₆H₂); ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ 19.96 (s, 2C, CH₃), 20.80 (s, 1C, CH₃), 20.83 (s, 1C, CH₃), 21.36 (s, 1C, CH₃), 21.43 (s, 1C, CH₃), 69.92 (m, 1C, C(CF₃)₂), 120.32 (q, ¹J_{C,F} = 278.32 Hz, 1C, CF₃), 122.14 (q, ¹J_{C,F} = 288.39 Hz, 2C, CF₃), 124.32 (m, 1C, CF₃C=CF), 124.58 (d, ²J_{C,F} = 32.96 Hz, 2C, Ar), 124.90 (d, ²J_{C,F} = 33.01 Hz, 1C, Ar), 128.96 (s, 2C, Ar), 129.43 (s, 2C, Ar), 138.54 (s, 2C, Ar), 139.52 (s, 2C, Ar), 141.40 (1C, Ar), 141.50 (1C, Ar), 143.00 (d, ¹J_{C,F} = 271.0 Hz, 1C, C=CF–C), 156.85 (d, ¹J_{C,F} = 356.14 Hz, 1C, N=C–F), 156.96 (dd, ¹J_{C,F} = 353.39 Hz, ⁴J_{C,F} = 6.41 Hz, 1C, N=C–F); ¹⁹F NMR (84 MHz, CDCl₃, 20 °C): δ –125.86 (m, 1F, C=C(F)–C), –71.34 (dd, ⁴J_{C,F} = 10.95 Hz, ⁵J_{C,F} = 10.95 Hz, 6F, 2CF₃), –64.08 (dd, ⁴J_{C,F} = 20.08 Hz, ⁵J_{C,F} = 10.96 Hz, 3F, CF₃), 4.56 (br s, 1F, C–C(F)=N), 4.99 (br s, 1F, C–C(F)=N).

2.1. X-ray determination of 5

Suitable crystals were obtained after recrystallization from hexane. CCDC-635821 C₂₆H₂₂F₁₂N₂, *M* = 590.16, monoclinic, *a* = 12.9146(6), *b* = 16.3564(9), *c* = 13.2829(6) Å, β = 109.626(3)°, *U* = 2642.8(2) Å³, *T* = 273(2) K, space group *P*2(1)/*n*, *Z* = 4, μ(Mo–K_α) 0.147 mm^{–1}, 15972 reflections measured, 5702 unique (*R*_{int} = 0.0251). The final *R*₁ = 0.0444, *wR*(*F*₂) 0.1341 for observed reflections (*I* > 2σ(*I*)). These data can be obtained free of charge from the Cambridge Crystallo-

graphic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References and notes

- Burton, D. J.; Naae, D. G.; Flynn, R. M.; Smart, B. E.; Brittelli, D. R. *J. Org. Chem.* **1983**, *48*, 3616–3618.
- Canac, Y.; Conejero, S.; Soleihavoup, M.; Donnadiou, B.; Bertrand, G. *J. Am. Chem. Soc.* **2006**, *128*, 459–464.
- Vignolle, J.; Donnadiou, B.; Bourissou, D.; Soleihavoup, M.; Bertrand, G. *J. Am. Chem. Soc.* **2006**, *128*, 14810–14811.
- Shevchenko, I.; Rogalyov, A.; Rozhenko, A.; Röschen-thaler, G.-V. *Eur. J. Inorg. Chem.* **2007**, 254–258.
- Burger, K.; Goth, H.; Höhenberger, W. *Chem. -Ztg.* **1977**, *101*, 453–454.
- Fergus, S.; Eustace, S. J.; Hegarty, A. F. *J. Org. Chem.* **2004**, *69*, 4663–4669.
- Burger, K.; Einhellig, K.; Süß, G.; Gieren, A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 156.
- Marion, N.; González, S. D.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988–3000.
- Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534–541.
- Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617*–618, 70–80.
- Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309.
- Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed.* **1996**, *35*, 1121–1123.