Ambident Reactivity of Bis(Diisopropylamino)carbene

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Bis(diisopropylamino)carbene can display not only carbenelike reactivity but also enter 1,3-addition reactions with the N unit.

Introduction

Except steric protection, the stability of singlet carbenes known to date is accounted for by π -electronic interaction of the vacant p_{π} orbital of the carbene center with the lone pair of electrons on adjacent phosphanyl and/or amino groups.^[1,2] For phosphanyl-stabilized carbenes this interaction can be schematically represented by the superposition of mesomeric structures **A**, **B**, and **C**. Theoretical calculations^[3] and X-ray diffraction studies^[4] revealed that the real structure is better described by zwitterionic form **B** with certain contributions of carbene **A** and phosphaacetylene **C**. Due to their electronic structure, phosphanylcarbenes can display the reactivity of carbenes as well as that of zwitterions with participation of the phosphorus atom.^[2]



Unlike phosphorus, nitrogen possesses stronger σ -accepting ability. Besides this, nitrogen adopts the planar configuration much more easily and the overlap of its lone pair of electrons with the p π orbital of the carbene carbon is more efficient.^[5,6] As a consequence, the amino group is a more effective π -donor. The stabilization of diaminocarbenes can be represented mainly by mesomeric structure **A**. The contribution of ylidic mesomeric form **B** was a matter of discussion.^[2,7] Alder and co-workers described the first acyclic stable bis(diisopropylamino)carbene and found that C–N bonds in this compound have as much double bond character as those in the appropriate amidinium ion.^[8] However, in all reactions known so far diaminocarbenes displayed only carbene-like behavior. In this paper, we

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 E-mail: igorshevchenko@yahoo.com would like to report on the first reaction of bis(diisopropylamino)carbene in which the N–C–N carbon atom takes part in the reaction together with one of the adjacent nitrogen atoms.

Results and Discussion

There are two examples known of the interaction of singlet nucleophilic diaminocarbenes with a carbonyl group.^[9,10] One of them is the reaction of bis(diisopropylamino)carbene (2) with aroylimines.^[9] Carbene 2 deoxygenates aroylimine 1 first to give carbene-nitrile ylide 3. This intermediate then reacts with a second equivalent of the carbene to afford alkene 4. This is a rare example of the untypical carbene-like behavior of 3. Compounds of this type usually react as nitrile ylides entering different 1,3-addition reactions.^[11]

We have found that together with alkene 4 the interaction of aroylimine 1 with carbene 2 leads to the formation of product 5 in 15% yield (Scheme 1). In this compound, both the carbon atom of the starting carbene and the adjacent nitrogen atom are enclosed in the heterocyclic five-membered ring. The formation of this [2+3] cycloaddition product implies that carbene 2 and carbene-nitrile ylide 3 can react with each other not only as two carbenes to give 4, but formally also as two zwitterions.

Compound **5** was isolated by column chromatography as a stable crystalline product. X-ray single-crystal analysis gave the molecular structure shown in Figure 1. The C9– C8 bond formed during the cyclization between the former carbene center and the hexafluoroisopropyl unit is very long (1.61 Å) and is comparable with the longest C–C bonds known.^[12] This can probably be accounted for by the repulsion of the sterically demanding diisopropylamino group and the two trifluoromethyl groups. The N2 nitrogen atom that initially belonged to the starting diaminocarbene is bound in compound **5** to the C7 atom of the former carbonyl group. This nitrogen atom has tetrahedral geometry and its lone pair of electrons is not conjugated with the adjacent C7–N1 double bond. Despite this and the presence

SHORT COMMUNICATION



Scheme 1.

of bulky substituents, the central five-membered ring is almost planar. It is interesting that the N2 atom in the starting bis(diisopropylamino)carbene was connected with two isopropyl groups but only one of them remained in product **5**. This means that the mechanism of the reaction should include elimination of one of the isopropyl groups before the formation of the N2–C7 bond. Such a transformation occurs probably through migration of one proton from the isopropyl group to the C9 atom with evolution of propene. A similar decomposition of the diisopropylamino group has been already observed in several carbenes.^[13–15]



Figure 1. Crystal structure of **5**. Selected bond lengths [Å] and angles [°]:C8–C9 1.610(2), N2–C7 1.367(2), C7–N1 1.287(2), C9–N2 1.4882(19), C9–N3 1.419(2), N2–C18 1.481(2); N1–C7–N2 118.16(14), C7–N2–C9 108.81(12), C10–C6–C1 107.16(12), N1–C7–N2–C9 –2.32, N1–C8–C9–N2 4.68, C9–C8–N1–C7 –6.18.

One can propose two possible reaction mechanisms for the formation of compound **5** depending on whether transformation of the diisopropylamino group with evolution of propene takes place before the formation of the C9–C8 bond or after it (Scheme 2). In the first case (mechanism A) carbene 2 should undergo decomposition to give imine 6, which then enters a 1,3-addition reaction with nitrile ylide 3 to give cyclic product 5.



Scheme 2.

However, there are some arguments because of which the initial decomposition of carbene 2 before reacting with 3 seems to be less probable. First, carbene 2 has been investigated in different reactions as a reagent or a catalyst and has displayed no tendency to such decomposition. Second, we did not detect a noticeable amount of compounds of type 5 when carbene 2 reacted with an aroylimine 1 containing the *p*-nitrophenyl group (Ar = p-NO₂C₆H₄) or the more sterically demanding mesityl group (Ar = Mes). Only the corresponding alkenes of type 4 were formed.^[9] Such a dependency of the formation of 5 on the nature of the Ar substituent can be observed only if the elimination of one isopropyl group occurs after the formation of the C9-C8 bond and not before it. Thus, it is probably more likely that the reaction begins with the formation of the C9-C8 bond to give intermediate compound 7 (mechanism B). Taking into account the considerable length of this bond, the process may have reversible character. The positively charged immonium center in 7 initiates a 1,3-proton shift that is followed by evolution of propene and closure of the ring. The impossibility of the cyclization of 7 if $Ar = p - NO_2C_6H_4$ or Mes is probably accounted for by the decreasing nucleophilicity of the C7 atom or by steric factors, respectively.

Conclusions

Reacting with each other, both diaminocarbene 2 and nitrile ylide 3 display ambident chemical behavior. The formation of compounds 5 and 4 means that diaminocarbene 2 does not only display carbene-like reactivity and that nitrile ylide 3 can also react like a mesomeric carbene species.

Experimental Section

General: All operations were performed under an atmosphere of nitrogen in a dry box. The solvents were dried by the usual pro-



cedures. The NMR spectra were recorded with Varian Gemini 400 MHz and JEOL FX-90Q spectrometers. The ¹H and ¹³C chemical shifts are referenced to tetramethylsilane (TMS), and the ¹⁹F shifts are referenced to CFCl₃. The ³¹P chemical shifts were measured by using 85% aqueous H_3PO_4 as an external standard.

Compound 5: To a frozen (-196 °C) solution of 2 (84 mg, 0.4 mmol) in Et₂O (1 mL) was dropwise added a chilled solution of N-(perfluoroprop-2-ylidene)benzamide (1; 52 mg, 0.19 mmol) in Et_2O (0.4 mL) so that the mixture remained solid. The mixture was warmed to room temperature over 20 min whilst stirring. After evaporation of ether in vacuo, the residue was extracted with hexane (1 mL) at 20 °C with stirring. The hexane solution was separated and stored overnight at -15 °C. After separation of the precipitate, the mother liquor was concentrated and purified by column chromatography ($R_{\rm f} = 0.6$, silica gel 60, hexane/diethyl ether, 10:1). Colorless crystals of 5 suitable for X-ray analysis were grown from hexane at 20 °C. Yield after recrystallization: 6 mg (7.5%). M.p. 116–117 °C. ¹H NMR (CDCl₃): $\delta = 0.88$ (d, ³ $J_{H,H} = 6.84$ Hz, 3 H, *i*Pr), 1.10–1.21 (m, 15 H, *i*Pr), 3.34 (sept., ${}^{3}J_{H,H} = 6.84$ Hz, 1 H, *i*Pr), 3.44 (sept., ${}^{3}J_{H,H} = 6.84$ Hz, 1 H, *i*Pr), 3.65 (sept., ${}^{3}J_{H,H} =$ 6.84 Hz, 1 H, iPr), 5.23 (s, 1 H, CH), 7.41-7.51 (m, 5 H, Ar) ppm. ¹³C NMR (CDCl₃): δ = 21.26 (s, 1 C, *i*Pr), 22.74 (s, 1 C, *i*Pr), 23.26 (s, 1 C, iPr), 23.67 (s, 1 C, iPr), 23.73 (s, 1 C, iPr), 24.44 (s, 1 C, *i*Pr), 30.13 (s, 1 C, N-C-N), 44.55 (s, 1 C, *i*Pr), 47.53 (s, 1 C, *i*Pr), 47.77 (s, 1 C, *i*Pr), 78.03 (br., 1 C, CF₃-C-CF₃), 122.99 (q, J_{C,F} = 283.81 Hz, 1 C, CF₃), 124.44 (q, $J_{C,F}$ = 282.28 Hz, 1 C, CF₃), 128.18 (s, 1 C, Ar), 128.62 (s, 1 C, Ar), 130.05 (s, 1 C, Ar), 133.28 (s, 1 C, Ar), 171.35 (s, 1 C, C=N) ppm. ¹⁹F NMR (CDCl₃): δ = -74.94 (q, ${}^{4}J_{\text{F,F}}$ = 10.38 Hz, 3 F, CF₃), -67.71 (q, ${}^{4}J_{\text{F,F}}$ = 10.38 Hz, 3 F, CF₃) ppm.

Crystal Data for 5: Data were collected with a Bruker Smart Apex II Enraf–Nonius CAD4 diffractometer. $C_{20}H_{27}F_6N_3$, M = 423.45, monoclinic, a = 9.4370(2) Å, b = 16.3176(5) Å, c = 13.8192(3) Å, $\beta = 95.267(2)^\circ$, V = 2119.02(9) Å³, T = 273(2) K, space group $P2_1/n$, Z = 4, μ (Mo- K_a) = 0.116 mm⁻¹, $\lambda = 0.71073$ Å, 13679 reflections measured, 5199 unique ($R_{int} = 0.0011$). Final *R* indices $R_1 = 0.0475$, w $R(F^2) = 0.1092$ [for 3161 reflections with I/ $\sigma(I) > 2.0$]. CCDC-637870 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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