NEW EXAMPLES OF CYCLOADDITION REACTIONS INVOLVING 2-DIALKYLBORYLAMINOPYRIDINES

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UDC 542.955:547.1'127:547.822.7

Borylated α -amino-N-heterocycles may undergo attack of a reagent possessing a double bond not only at the 1,2 positions (i.e., at the B-N bond) but also at the 1,4 positions (i.e., at the boron atom and the terminal nitrogen atom). However, only a few examples of the latter reactions have been reported. Dialkylboryl derivatives of 2-aminopyridine (DBAP) form (4 + 2)-cycloadducts with isocyanates and isothiocyanates [1, 2]. The reaction of isocyanates on 2-dialkylborylaminothiazoles leads to compounds with analogous structure [3]. In our recent work [4], we have shown that ethoxyacetylene also added to DBAP at the 1,4 positions.

In the present work, we continued our search for new cycloaddition reactions involving DBAP. We might have assumed that other heterocumulenes such as carbodimides are capable, similar to isocyanates and isothiocyanates, of forming cycloadducts with DBAP. In fact, the behavior of DBAP towards carbodimides is not clearcut. As previously established, DBAP reacts with dicyclohexylcarbodimide (DCHC), in contrast to RNCO and RNCS, with cleavage of the B-N bond [2, 5]. In an attempt to obtain the (4 + 2)-cycloadduct from dibutylborylamino-pyridine (I) and diphenylcarboddimide (DPC), we isolated colorless crystals of bicyclic compound (II), which is analogous in structure to the chelates synthesized from DBAP and DCHC



On the other hand, 2-diisopropylborylaminopyridine (III) reacts with DPC at about 25° C to form a bright yellow product, (IV), which is the (4 + 2) cycloaddition product.



We may assume that the sharp difference in the behavior of DBAP (I) and (III) relative to DPC is a function of steric factors. The branched alkyl groups at the boron atom are likely responsible for the hindrance to formation of the four-centered transition state [see scheme (1)] to a greater extent than the in the six-centered transition state [scheme (2)]. Thus, reaction (2) with the formation of (4 + 2)-cycloadduct (IV) is more favored for (III) containing an i-Pr₂B group.

Reaction (2) is reversible in nature: heating (IV) above 70-90°C leads to its decomposition at a significant rate to give (III) and DPC. A further increase in temperature under conditions of equilibrium between (IV) and the starting reagents gives the irreversible 1,2-addition of (III) at the C=N bond of DPC (by analogy to scheme (1)), i.e., (IV) smoothly

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1139-1143, May, 1987. Original article submitted June 9, 1986. isomerizes to chelate (V) which is analogous in structure to (II) (scheme (3)).



The conversion of (IV) to (V) is apparently to the type of thermal rearrangements found in our earlier work on the isomerization of the (4 + 2)-cycloadducts obtained from DBAP and iso-cyanates [6]. Chelate (IV) is decomposed by water and alcohols upon heating. In the air, (IV) is decomposed by water and alcohols upon heating. In the air,

A delocalized π -electron system in the chelate ring is characteristic for (II) and (V) as for the chelates obtained from DBAP and DCHC [5]. Their IR spectra lack absorption at 1630-1700 cm⁻¹, while the IR spectrum of (IV) has a vC=N band at 1670 cm⁻¹. The delocalization accounts for the considerable chemical and thermal stability of (II) and (V) in comparison with (IV). The boron-containing ring in (II) and (V) is not cleaved by ethanol at reflux in the presence of HCl. In ether, the action of HCl on (II) leads to the formation of boronium salt (VI).



A study of the reaction of DBAP and nitriles showed that the result in this case also depends on the choice of reagents. In our previous work [7], we note that (III) reacts with an activated nitrile, namely, malonitrile (VII), by (4 + 2)-cycloaddition to form bright yellow crystalline chelate (VIII). An attempt to obtain the analogous products from (I) and (VII) was not successful.



The vC=N band in the IR spectrum of (VIII) has a relatively low frequency (2184 cm⁻¹), which indicates an NC-CH=C- conjugated system. The absorption of the C=N group corresponds to the band at 1667 cm⁻¹. As in the case of (4 + 2)-cycloadduct (IV), (VIII) is thermally and chemically unstable (especially in solution) but may be stored unchanged over several weeks preventing contact with air.

We were then able to show that DBAP derivatives are also capable of undergoing (4 + 1) cycloaddition. The action of phenyl isocyanide (I) in hexane leads to bright yellow crystalline chelate (IX), in which the boron atom is in a five-membered ring:



The IR spectrum of (IX) has vC=N band at 1660 cm⁻¹. Upon heating, chelate (IX), similarly to (IV) and (VIII), decomposes to give the starting reagents and cannot be stored in the air.

EXPERIMENTAL

The operations with the organoboron compounds were carried out in a dry argon atmosphere. DBAP (I) and (III) were obtained according to our previous procedure [8]. DPC was obtained according to Pornet and Maginiac [9]. The ¹¹B NMR spectra (δ , ppm) were obtained on a Bruker AM-300 spectrometer with Et₂0·BF₃ as the external standard. The IR spectra (ν , cm⁻¹) were taken on a UR-20 spectrometer. The mass spectra (m/z) were taken on a Variant MAT CH-6 mass spectrometer with direct sample inlet into the ion source.

 $[N^{1}-(Pyrid-2-y1)-N^{2}, N^{3}-diphenylguanidinato]dibutylboron (II). A sample of 6.92 g DPC in 10 ml hexane was added dropwise at 25°C to 6.39 g (I) in 25 ml hexane. The crystals which precipitated out after several days were filtered off and washed with hexane to give 8.78 g (60%) chelate (II), mp 81-84°C. Found: C, 75.88; H, 8.08; B, 2.92; N, 13.23%. Calculated for C₂₆H₃₃BN₄: C, 75.72; H, 8.06; B, 2.62; N, 13.59%. Mass spectra: 355 [M - Bu]⁺, 161 [M - Bu - (PhN=C=NPh)]⁺. ¹¹B NMR spectrum in THF: 3.0. IR spectrum in CHCl₃:3422 (NH).$

[1-(N,N'-Diphenylamidino)pyridon-2-iminato]diisopropylboron (IV). A sample of 8.31 g DPC in 10 ml hexane was added dropwise to 8.10 g (III) in 25 ml hexane. The crystalline precipitate was filtered off and washed with hexane to give 12.0 g (74%) chelate (IV), mp 93-97°C (dec.). Found: C, 75.30; H, 7.94; B, 2.88; N, 14.66%. Calculated for $C_{24}H_{29}BN_4$: C, 75.02; H, 7.61; B, 2.82; N, 14.58%. ¹¹B NMR spectrum in THF: 1.2. IR spectrum in CHCl₃: 1670 (C=N), 3410 (NH).

 $\frac{[N^{1}-Pyrid-2-yl]-N^{2},N^{3}-diphenylguanidinato]diisopropylboron (V).}{Was heated at 100-150° for 2 h. The product was transferred to a filter and washed with hexane to give 4.5 g (96.5%) chelate (V), mp 110-111°C (from hexane). Found: C, 75.24; H, 7.73; B, 3.04%. Calculated for <math>C_{24}H_{29}BN_{4}$: C, 75.02; H, 7.61; B, 2.82%. Mass spectrum: 341 $[M - i-Pr]^{+}$, 147 $[M - i-Pr - (PhN=C=NPh)]^{+}$. ¹¹B NMR spectrum in THF: 4.1. IR spectrum in CHCl₃: 3422 (NH).

Salt (II) HCl (VI). Ethereal 3.38 N HCl (1.27 ml) was added to a solution of 1.76 g (II) in 30 ml ether. The white crystalline precipitate was filtered off and washed with ether to give 1.90 g (99%) salt (VI), mp 173-180°C. Found: C, 69.81;H, 7.67; B, 2.26; Cl, 8.36%. Calculated for $C_{26}H_{34}BClN_4$: C, 69.57; H, 7.64; B, 2.41; Cl, 7.90%.

[1-(α-Amino-β-cyanovinyl)pyridon-2-iminato]diisopropylboron (VIII). A sample of 2.0 g (III) was added to 0.7 g (VII) in 13 ml benzene and the mixture was maintained for 24 h. The crystalline precipitate was filtered off and washed with benzene to give 2.43 g (83%) chelate (VIII), mp 102-110°C (dec.). Found: C, 65.76; H, 8.36; B, 3.84%. Calculated for $C_{14}H_{21}BN_4$: C, 65.64; H, 8.26; B, 4.22%. Mass spectrum: 213 [M - Pr]⁺, 147 [M - Pr - (NCCH₂CN)]⁺. ¹¹B NMR spectrum in THF: -2.6. IR spectrum in CHCl₃: 2184 (C=N), 3390, 3407 (NH).

[1-(N-Phenyl)formamidoylpyridon-2-iminato-C,N]dibutylboron (IX). A sample of 6.5 g PhNC was added dropwise to 12.7 g (I) in 20 ml hexane. The crystalline precipitate was filtered off and washed with hexane to give 16.3 g (87%) (IX), mp 92-97°C (dec.). Found: C, 74.71; H, 8.83; B, 3.59%. Calculated for $C_{20}H_{28}BN_3$: C, 74.77; H, 8.78; B, 3.37%. ¹¹B NMR spectrum in CH_2Cl_2 : -4.7. IR spectrum in KBr: 1658 (C=N), 3350 (NH). IR spectrum in CHCl₃: 3447 (NH).

CONCLUSION

1. 2-Diisopropylborylaminopyridine undergoes cycloaddition with diphenylcarbodiimide and malononitrile, while 2-dibutylborylaminopyridine undergoes the analogous reaction with phenyl isocyanide.

2. [1-(N,N'-Diphenylamidino)pyridon-2-iminato]diisopropylboron (IV) undergoes thermal isomerization to [N¹-(pyrid-2-yl)-N²,N³-diphenylguanidinato]diisopropylboron (V).

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SOME PROPERTIES OF THE ADDUCT OF BENZENESULFINYL CHLORIDE WITH MYRCENE

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At high pressure, PhSOC1 reacts with isoprene (Ia) to give Z-chlorosulfoxide (IIa) [1]. The replacement of (Ia) by triene (Ib) leads to the analogous result: at 5 kbar, myrcene forms labile chlorosulfoxide (IIb) whose structure was confirmed by spectral analysis and conversion to stable products. Thus, the PMR spectrum of chloride (IIb) has characteristic signals for the trans- and cis-CH₃ groups of the isopropylidene fragment at $\delta \sim 1.6$ and 1.7 ppm. The signals for the CH₂S protons form an AB spectrum with $J_{AB} = 12$ Hz which coincides with that found for isoprene derivative (IIa) [1].



The acetolysis of chlorosulfoxide (IIb) by KOAc in acetic acid leads to acetate (III). The reduction of (III) by $LiAlH_4$ gives hydroxysulfide (IV). The hydrolysis of (IV) gives hydroxy derivative (V).

The structures of (III)-(V) were confirmed by their physical data and elemental analysis results. Treatment of hydroxysulfoxide (V) by Na/NH_3 gave geraniol (VI) in about 70% yield. The formation of about 10% nerol may be attributed to the partial isomerization of the trisubstituted C=C bond in the allyl carbanion arising under the Birch reduction conditions.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in $CHCl_3$. The PMR spectra of the solutions in $CDCl_3$ were taken on a Tesla BS-497 spectrometer at 100 MHz and Bruker WM-250 spectrometer relative to TMS. The mass spectra were taken on a Varian MAT CH-6 spectrometer at 70 eV. The R_f values were given for Silufol silica gel plates.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1143-1145, May, 1987. Original article submitted June 13, 1986.

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