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Evidence for Imidoylnitrene Intermediates in the Reaction of Bromophenyldiazirine with Phosphines: First Ring-Expansion Reaction of a Diazirine

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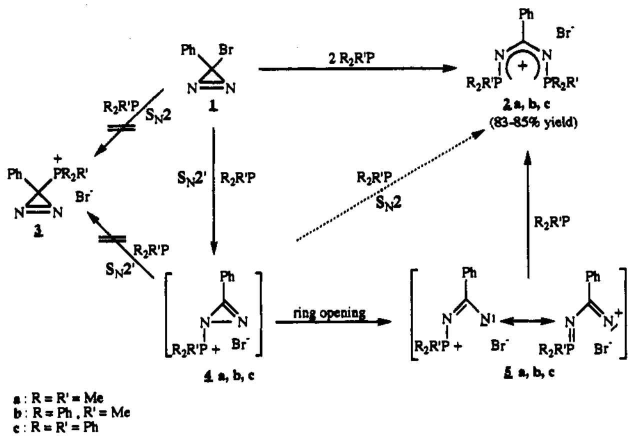
In contrast with their acyclic isomeric diazo compounds,[1] diazirines[2] tolerate a variety of heteroatom substituents and, therefore, are valuable precursors for different carbenes, especially nucleophilic carbenes.[3] The exchange reaction of nucleophiles with the easily available halodiazirines[4] is the key point in the synthesis of these heterocycles. The mechanism of this reaction has been a highly controversial topic in the last few years.[3,5] It was first suggested that the halodiazirine was in equilibrium with a diazirinium cation, which was captured by the nucleophiles.[1a,3,4,6] From the observed products, Creary[7] and Dailey,[8] using a ^{15}N-labeled diazirine, independently concluded that the first step of the reaction with azide anion involved an S_N2' mechanism, and it was suggested that the exchange reaction with other nucleophiles proceeded by a double S_N2' reaction.[9] Lastly, Creary demonstrated that, in the presence of light, azide ion can react with certain halodiazirines via an $S_{RN}1$ substitution mechanism.[10]

Here we report preliminary results on the reaction of bromophenyldiazirine **1** with phosphines.[11] These nucleophiles have been chosen since ^{31}P NMR spectroscopy is a powerful tool for monitoring the reactions, and we have already shown that organophosphorus substituents allowed the stabilization of highly reactive species.[12]

Two equivalents of trimethyl-, diphenylmethyl-, and triphenylphosphine react in dichloromethane with bromophenyldiazirine **1**,[4] affording the bis adducts **2**,[13] in near quantitative yields; when a stoichiometric amount of phosphine is used, **2** is also formed and half of the starting diazirine **1** is recovered. Monitoring the reaction by ^{31}P NMR spectroscopy, at low temperature, does not allow the detection of any intermediates. The rate of the reaction increasing with the nucleophilicity of the phosphines and the resulting products **2** featuring a P–N bond, and not a P–C bond, as in **3**, clearly demonstrate that the first step is an S_N2' reaction leading to 1*H*-diazirine **4**. Two mechanisms could rationalize the formation of the second P–N bond: either an S_N2 reaction of the phosphine on the second nitrogen atom induced by the presence of the electron-withdrawing phosphonio group or the formation of an electrophilic imidoyl nitrene **5** which would be trapped by phosphines.[14] Since there is no precedent for the S_N2 mechanism, while the ring-opening of 1*H*-diazirines into imidoyl nitrenes has already been postulated to rationalize the formation of carbodiimides or related products from nitrilimines,[15] we favor this later mechanism[16] (Scheme 1).

Scheme 1



In order to confirm this hypothesis, we performed the reaction of **1** with a stoichiometric amount of bis(diisopropylamino)-(trimethylstannyl)phosphine. Indeed, the tin–phosphorus bonds are very labile, and one could expect the elimination of bromotrimethylstannane from *N*-phosphoniodiazirine **4** leading to *N*-phosphinodiazirine **6**. Then, the corresponding imidoyl nitrene **7** could intramolecularly react with the phosphorus atom, leading to the hitherto unknown 1,3,2λ^5-diazaphosphete **8**.[17] Indeed, this cyclic 4-π-electron ylide **8** was isolated in 26% yield;[18] ((trimethylstannyl)imino)bis(diisopropylamino)bromophosphorane **11** (32% yield),[18] benzonitrile (35% yield according to gas chromatography), bromotrimethylstannane (60% yield, according to ^{1}H NMR spectroscopy) and uncharacterized byproducts were also formed in the reaction (Scheme 2).

Compared with the reaction of **1** with azide ion,[7,8] here benzonitrile is also obtained, but instead of eliminating N_2, it is quite likely that there is formation of λ^3-phosphinonitrene–λ^5-

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(13) **2a**: mp 170–171 °C; 85% yield; ^{31}P NMR ($CDCl_3$) +30.1; ^{13}C NMR ($CDCl_3$) 14.6 (d, J_{PC} = 66.4 Hz, CH_3), 140.7 (t, J_{PC} = 12.7 Hz, C_{ipso}), 178.1 (t, J_{PC} = 7.2 Hz, NCN). **2b**: mp 177 °C, 85% yield; ^{31}P NMR ($CDCl_3$) +20.1; ^{13}C NMR ($CDCl_3$) 13.4 (d, J_{PC} = 66.1 Hz, CH_3), 140.0 (t, J_{PC} = 11.6 Hz, C_{ipso}), 179.4 (t, J_{PC} = 6.1 Hz, NCN). **2c**: mp 101 °C; 83% yield; ^{31}P NMR ($CDCl_3$) +16.6; ^{13}C NMR ($CDCl_3$) 139.3 (t, J_{PC} = 12.0 Hz, C_{ipso}), 178.6 (t, J_{PC} = 6.2 Hz, NCN).

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(18) **8**: white crystals, mp 136–138 °C (1.6 g, 26% yield); ^{31}P NMR ($CDCl_3$) +54.2; ^{13}C NMR ($CDCl_3$) 22.1 (s, CH_3), 47.2 (d, J_{PC} = 4.3 Hz, CH), 126.6 128.2, 130.8 (s, $C_{o,m,p}$), 136.1 (d, J_{PC} = 22.4 Hz, C_{ipso}), 194.7 (d, J_{PC} = 48.4 Hz, NCN). **11**: pale yellow oil; ^{31}P NMR (C_6D_6) −11.8; ^{1}H NMR ($CDCl_3$) 0.41 (s, $J_{^{119}SnH}$ = 55.0 Hz, $J_{^{117}SnH}$ = 57.6 Hz, CH_3Sn).

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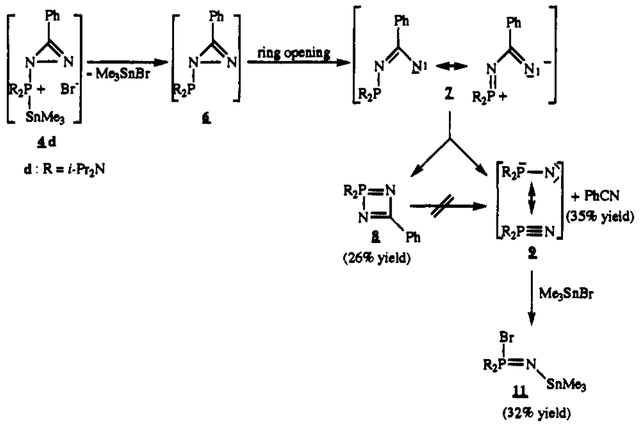
Scheme 2



phosphonitrile **9**,[19] which is trapped, by the bromotrimethylstannane formed in the reaction, affording **11**. We have checked that phosphonitrile **9**, generated by photolysis of bis(diisopropylamino)phosphinous azide,[19] reacts with the bromostannane to give **11**; moreover, when the reaction of **1** with the stannylphosphine was carried out in the presence of a large excess of chlorotrimethylsilane, we observed (in addition to **8**, benzonitrile, bromotrimethylstannane, and a very small amount of **11**) the formation of ((trimethylsilyl)imino)bis(diisopropylamino)-chlorophosphorane.[19]

These results, as a whole, clearly confirm that, in the bromophenyldiazirine exchange reactions, the first step involves an S_N2' mechanism leading to N-substituted diazirines; they confirm the possible ring-opening of these heterocycles into imidoyl nitrenes, which can either be trapped inter- or intramolecularly or decompose into nitrile and a nitrene fragment. The presence of a phosphonio group, which is a strong electron-withdrawing group, should induce a loss of antiaromatic character and therefore stabilize the N-substituted diazirine; moreover, the phosphines are excellent leaving groups. Thus, it is really surprising that the expected second S_N2' reaction, which would have led to the *C*-phosphoniodiazirine **3**, does not occur. In contrast to the small anions like MeO^- or F^-, the phosphino groups are very poor migrating groups, and one can question if what was believed to be an S_N2' reaction is not in fact a 1,3-sigmatropic reaction.

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