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CONTRASTING THERMAL REACTIONS OF ALLYLIC SULFILIMINES AND PHOSPHINIMINES

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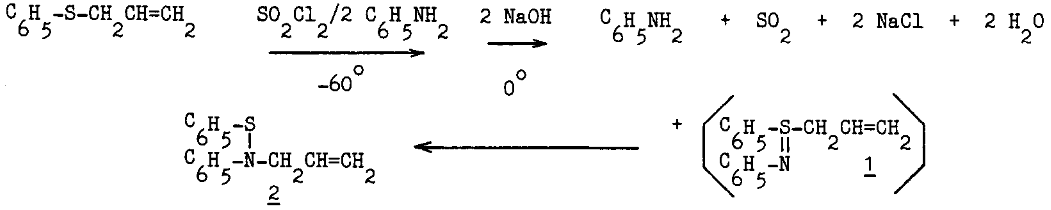
Summary: Allylic sulfilimines and phosphinimines undergo spontaneous but contrasting rearrangements at low temperatures. Whereas a sulfilimine is converted to an isomeric sulfenamide by (2,3)-sigmatropic rearrangement, a structurally analogous phosphinimine undergoes an unusually facile double bond shift to form an isomeric vinylic structure.

The (2,3)-sigmatropic rearrangement process, employed in appropriate allylic systems, can be used to directly examine the relative stabilities of "linear" vs. "branched" isomeric forms, such as sulfenates and sulfoxides.[1] In the present study, this approach has been applied, for the first time, to permit a direct comparison of the behavior of allylic sulfilimines and phosphinimines.

Following a standard approach,[2] N-phenyl allylphenylsulfilimine, 1 , was prepared from the corresponding allylphenylsulfide (Scheme A). The sulfide was treated, at -60°C in methylene chloride, with sulfuryl chloride followed by aniline. The resulting aminosulfonium salt was then treated further, at 0°, with aqueous sodium hydroxide. The product isolated from this reaction was shown by ^{1}H-NMR analysis (α CH$_2$: $\delta = 4.3$, d $^{HH}J = 7$ Hz) and by independent synthesis[3] to be N-allyl-N-phenyl benzenesulfenamide, 2 , revealing that (2,3)-allylic rearrangement of the initially formed sulfilimine, 1 , occurs readily under these conditions. The fact that the linear sulfenamide, 2 , is preferred energetically to the branched sulfilimine, 1 , confirms[4] that, in this respect, sulfilimines resemble thiosulfoxides (where rearrangement to linear disulfides is favored[5]) rather than sulfoxides (which are generally favored over the isomeric, linear sulfenates[1]).

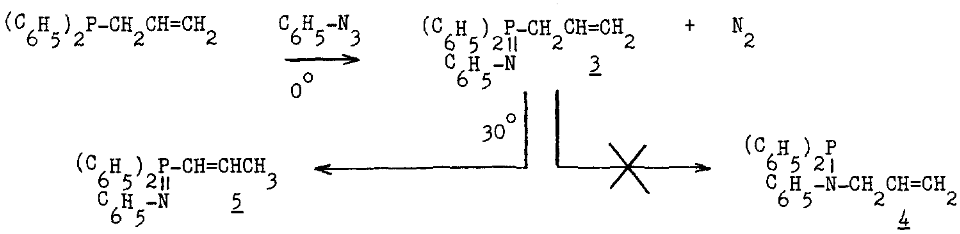
Scheme A



$$C_6H_5\text{-S-}CH_2CH{=}CH_2 \xrightarrow[-60^\circ]{SO_2Cl_2/2\ C_6H_5NH_2} \xrightarrow[0^\circ]{2\ NaOH} C_6H_5NH_2 + SO_2 + 2\ NaCl + 2\ H_2O$$

To permit comparison of these results with a structurally analogous phosphorus system, N-phenyl allyldiphenylphosphinimine, 3 , was synthesized. This product was obtained upon treatment of allyldiphenylphosphine with phenyl azide in benzene, at 0° (Scheme B).[6] Under these conditions, the phosphinimine, 3 , is sufficiently stable to permit direct spectral analysis (α CH$_2$: δ = 3.4, dd ^{HH}J = 7 Hz, ^{PH}J = 14 Hz) and to confirm that in contrast to sulfilimine, 1 , (2,3)-allylic rearrangement to the isomeric aminophosphine, 4 , is not observed. In its apparent preference for the branched isomeric form, the phosphinimine resembles the behavior of allylic phosphine oxides[7] and sulfides.[8]

Scheme B



Upon being monitored in solution at 30°, phosphinimine 3 does, in fact, undergo a spontaneous rearrangement. However, this does not involve the (2,3)-allylic rearrangement; rather, an unexpected and unusually facile double bond shift converts the allylic structure, 3 , to an isomeric vinylic one, 5 , N-phenyl 1-propenyldiphenylphosphinimine (γ CH$_3$: δ = 2.0, dd ^{HH}J = 5 Hz, ^{PH}J = 2 Hz). This transformation occurs cleanly and was examined by NMR in several solvents, using vacuum-sealed samples. The rearrangement half-lives are quite concentration dependent, and the reaction is accelerated by increasing solvent polarity. At approximately 1.5 M concentration in chloroform-d, for example, the reaction exhibits a half-life of roughly four hours at 30°.

In a comparison study, it was demonstrated that the corresponding allyldiphenylphosphine oxide is thermally stable up to at least 150°, although conversion to the more stable vinylic isomer, 1-propenyldiphenylphosphine oxide, was readily accomplished at 0°, employing basic catalysis by potassium t-butoxide in tetrahydronfuran. It appears that the more basic nitrogen of the phosphinimine (compared to oxygen in the phosphine oxide) greatly facilitates the proton shift sequence which is presumably involved in the allylic to vinylic rearrangement.

References and Notes

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2. P. Claus, W. Reider, P. Hoffbauer, and E. Vilsmaier, Tetrahedron 31 , 505 (1975).

3. Sulfenamide, 2 , was prepared by treatment of N-allylaniline with n-butyl lithium at -50°, followed by addition of benzenesulfenyl chloride.

4. Allylic N-arylsulfonyl and N-arylphosphoryl sulfilimines also undergo the (2,3)-sigmatropic rearrangement to form isomeric sulfenamides.
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