Valence isomerization of 2-phospha-4-silabicyclo[1.1.0]butane: a high-level ab initio study

Abstract The rearrangements for 2-phospha-4-silabicyclo[1.1.0]butane, analogous to the valence isomerization of the hydrocarbons bicyclobutane, 1,3-butadiene, and cyclobutene, were studied at the (U)QCISD(T)/6-311+G**/(U)QCISD/6-31G* level of theory. The monocyclic 1,2-dihydro-1,2-phosphasiletes are shown to be the thermodynamically preferred product, in contrast to the isomerization of the hydrocarbons, which favors the 1,3-butadiene structure. Furthermore, an unprecedented direct isomerization pathway to the 1,2-dihydro-1,2-phosphasiletes was identified. This pathway is competitive with the isomerization via the open-chain butadienes and becomes favorable when electron-donating substituents are present on silicon.

Keywords Heterobicyclobutanes · Valence isomerization · Ab initio theory

Introduction Bicyclo[1.1.0]butane with its strain energy of over 60 kcal mol\(^{-1}\) is a fascinating compound that has attracted the interest of both experimental and theoretical chemists [1]. It is now well established that bicyclo[1.1.0]butane (1) opens to the more stable valence isomer gauche-butadiene (2) by a pericyclic rearrangement, which is characterized by a concerted, asynchronous conrotatory ring opening where the central C–C bond remains intact [2, 3]. This is an allowed [\(\pi_2+\pi_2\)] conrotatory rearrangement according to the Woodward–Hoffmann (W–H) orbital-symmetry rules [4–6], affording kinetic intermediate 2 that can easily rotate to \(s\)-trans-1,3-butadiene (3). The activation barrier of 41.5 kcal mol\(^{-1}\) calculated at the multiconfiguration self-consistent field level of theory [2] agrees closely with the experimental value of 40.6 kcal mol\(^{-1}\) [7, 8]. The disrotatory, W–H forbidden, thermal ring opening of 1 is less favorable, and was calculated to be about 15 kcal mol\(^{-1}\) higher in energy [2]. Another rearrangement is also feasible; stretching of the central C–C bond leads to a planar singlet diradical transition structure for inversion, which is also a higher energy process with a barrier of 47.4 kcal mol\(^{-1}\) [9].

Valence isomer cyclobutene (4) is of intermediate stability between 1 and 3 and converts thermally to gauche-butadiene 2 by an electrocyclic ring opening [10, 11]. This pericyclic rearrangement follows a W–H allowed concerted, conrotatory pathway. The calculated activation barrier at the MP2/6-311G** level of theory of 33.7 kcal mol\(^{-1}\) [12–14] for this process is in agreement with the experimental value of 32.9 ± 0.5 kcal mol\(^{-1}\) [10, 11]. Usually for the ring opening of cyclobutenes, steric effects dominate the preference for inward versus outward rotation [15]. However, electronic effects can also dictate this rearrangement, as was reported very recently for the sterically hindered substrate 5, which prefers to react via the more crowded inward rotatory pathway, leading mainly to butadiene 6 (Scheme 1) [16, 17].
Bicyclo[1.1.0]butanes with main-group hetero-elements in the ring have also received considerable attention [18]. However, little is known about the phosphorus-containing analogues [19–22]. In our ongoing research on small strained organophosphorus ring systems, we became interested in the yet unknown 2-phospha-4-silabicyclo[1.1.0]butanes, whose occurrence we reported as a reactive intermediate recently [23, 24].

Valence isomerization of the 2-phospha-4-silabicyclo[1.1.0]butane to the 1,2-dihydro-1,2-phosphasiletes was indicated by reacting 1H-phosphirene with silylene Si[(NN)Si(NN)](Scheme 2).

SCS-MP2/6-311+G** calculations on B3LYP/6-31G* model structures show that the intermediate 2-phospha-4-silabicyclo[1.1.0]butane isomerizes directly, via an unprecedented W–H allowed process, to the thermodynamically preferred 1,2-dihydro-1,2-phosphasilete [23, 24]. This pathway is favored over the concerted, asynchronous conrotatory ring opening leading to s-trans-1-phospha-4-sila-1,3-butadiene [25].

Here, we report on the isomerization of 2-phospha-4-silabicyclo[1.1.0]butane A to its valence isomers 1-phospha-4-sila-1,3-butadiene B and 1,2-dihydro-1,2-phosphasilete C (only one other synthesis of 1,2-dihydro-1,2-phosphasiletes was reported: [26–28]), using high-level ab initio calculations at the (U)QCISD(T)/6-311+G**/(U)QCISD/6-31G* level of theory. We will compare the differences between a direct A → C pathway versus the isomerization via butadiene B. In addition, the influence of substituents on silicon on the rearrangements will also be discussed.

Computational details

All calculations were performed using the GAUSSIAN 98 [29] suite of programs. Geometries were optimized using the standard 6-31G* basis set at the (U)MP2 and (U)QCISD [30, 31] level of theory, while single-point calculations were preformed at the (U)QCISD(T)/6-311+G** level using the (U)QCISD/6-31G* geometries. First and second order energy derivatives were computed to confirm that minima or transition structures had been located at the (U)MP2/6-31G* level. Intrinsic reaction coordinate driving calculations were performed at the (U)MP2/6-31G* level to establish the connections between transition structures and minima. The total energies calculated at the (U)MP2, (U)QCISD, and (U)QCISD(T) levels were corrected for the (U)MP2/6-31G* level zero-point energies scaled by a factor of 0.967 [32].

Results and discussion

First, we investigated the rearrangements of bicyclo[1.1.0]butane (1) and cyclobutene (4) into the more stable s-trans-1,3-butadiene (3) at the (U)QCISD(T)/6-311+G**/(U)QCISD/6-31G* level of theory (this method gives similar energies when compared to the CASSCF(10,10)/6-31G* level of theory as was reported for the isomerization of 2-oxabicyclo[1.1.0]butane: [33]), since no complete study of the valence isomerizations of all C4H6 isomers at the same level of theory were reported to date. Subsequently, we investigated the rearrangements of the 2-phospha-4-silabicyclo[1.1.0]butanes, where the effects of heteroatom substitution on the characteristics of the rearrangements become apparent. Bicyclo[1.1.0]butane (1) leads to gauche-butadiene 2 via a concerted, asynchronous conrotatory ring opening [2, 3], which has a barrier of 39.2 kcal mol⁻¹, and is exothermic by 26.0 kcal mol⁻¹ (Fig. 1). This closed-shell rearrangement is favored over the corresponding...
39.2 kcal mol$^{-1}$ for the [$\sigma 2s + \sigma 2a$] process in bicyclo[1.1.0]butane (1). The closed-shell rearrangement $11 \rightarrow 12$ is favored over the corresponding diradical open-shell pathway ($\Delta E^r = 41.3$ kcal mol$^{-1}$, $<S^2^r> = 0.97$).

$s$-Trans-butadiene 12 can transform into the slightly less stable gauche-butadiene 13 ($\Delta E = 2.6$ kcal mol$^{-1}$) with an energy barrier of 7.5 kcal mol$^{-1}$. Subsequently, butadiene 13 can isomerize via a conrotatory electrocycl ring closure to the much more stable 1,2-dihydro-1,2-phosphasilene (14) ($\Delta E = -23.9$ kcal mol$^{-1}$), with a rearrangement barrier of only 3.2 kcal mol$^{-1}$. Clearly, if a 1-phospha-4-sila-butadiene is to be formed from 11, it will rearrange to the four-membered ring structure 14.

We conclude that in contrast to the hydrocarbons, where butadiene 3 is the favored product, the P,Si-derivatives 12 and 13 are not likely candidates to be observed on rearranging bicyclic compound 11.

As 14 is thermodynamically the preferred valence isomer, we also explored whether it could be formed directly from bicyclic 11. Indeed, forcing an asynchronous conrotatory ring opening with an initial SiH$_2$-group rotation resulted in a transition structure TS11–14 for the direct rearrangement of 11 into 14 (Fig. 4). The barrier of 39.0 kcal mol$^{-1}$ for this closed-shell process is similar to the conversion via the P,Si-butadienes ($\Delta E^r = 38.8$ kcal mol$^{-1}$, Fig. 3). The rearrangement via TS11–14 obeys the orbital symmetry rules and can be described as a [$\sigma 2s + \sigma 2a$] process. Such a pathway is unprecedented for the isomerization of the carbon analogue bicyclo[1.1.0]butane [1] [2], for which $s$-trans-1,3-butadiene is the favored product.

Due to the similarities in activation energy for the conversions $11 \rightarrow 12$ and $11 \rightarrow 14$ at the QCISD(T)/6-311+G**//QCISD/6-31G* level of theory, we have also incorporated in our computational model the cyclic diamine HN-C=C-NH as substituent on silicon to investigate the effect of donating N atoms, which are also present in our experimental system [23, 24] on the rearrangements.

$^{1}$No competitive open-shell rearrangement is present for TS11–14.
Subsequently, 17 can isomerize via a conrotatory electrocyclic ring closure to the much more stable 1,2-dihydro-1,2-phosphasilete 18 (\(\Delta E = -25.6\) kcal mol\(^{-1}\)) with a minute barrier of only 1.3 kcal mol\(^{-1}\). The geometrical parameters of the optimized 18 are in good agreement with the single-crystal X-ray analysis of 10a [23, 24]. Interestingly, the direct valence isomerization now becomes favorable, and 2-phospha-4-silabicyclo[1.1.0]butane 15 gives cyclobutene derivative 18 (\(\Delta E = -27.7\) kcal mol\(^{-1}\)) via a W–H allowed \([\sigma 2s+\sigma 2a]\) process, with an exothermicity of 25.6 kcal mol\(^{-1}\) (Fig. 6).

The lower barrier for the direct conversion 15 \(\rightarrow\) 18 compared to that of the parent 11 \(\rightarrow\) 14 can be ascribed to the presence of the donating amino groups on silicon. Generally, \(\pi\)-donor (e.g., NH\(_2\)) and \(\sigma\)-acceptor (e.g., F) substituents destabilize three-membered rings, making them more reactive, as indicated by their increased ring strain [38, 39]. This is also evident for the 15 \(\rightarrow\) 18 conversion by an increased exothermicity (\(\Delta E_{11} \rightarrow 14 = 21.7\) kcal mol\(^{-1}\); \(\Delta E_{15} \rightarrow 18 = 25.6\) kcal mol\(^{-1}\)). Additionally, the analogous rearrangement for the fluoro-substituted 2-phospha-4-silabicyclo[1.1.0]butane 19 confirms this trend (\(\Delta E_{19} \rightarrow 20 = 28.1\) kcal mol\(^{-1}\), Fig. 7). Furthermore, the associated transition state of this novel pathway is stabilized by the electron-donating \(N\)-heterocyclic substituent on silicon (\(\Delta E_{11} \rightarrow 14 = 39.0\) kcal mol\(^{-1}\); \(\Delta E_{15} \rightarrow 18 = 27.7\) kcal mol\(^{-1}\); \(\Delta E_{19} \rightarrow 20 = 35.0\) kcal mol\(^{-1}\)).

**Conclusions**

Hetero substitution changes the stability of the valence isomers of bicyclo[1.1.0]butane (1), 2-Phospha-4-silabicyclo[1.1.0]butane (11) is the least stable isomer and 1,2-dihydro-1,2-phosphasilete (14) the most stable one at the

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\(^{2}\)Open-shell TS15-16 was calculated at the UQCISD(T)/6-311+G**//UMP2/6-31G* level of theory.
Two reaction pathways for the thermal isomerization of 2-phospha-4-silabicyclo[1.1.0]butane (11) have been found: (a) a three-step process starting with a barrier of 38.8 kcal mol$^{-1}$ for the concerted, asynchronous conrotatory ring opening of 11 to $s$-trans-1-phospha-4-sila-1,3-butadiene (12), followed by a conformational change to the gauche isomer 13 and a subsequent conrotatory electrocyclic ring closure to 14, and (b) a direct transformation of 11 into 14 via a [$\sigma_2s+\sigma_2a$] process with a barrier of 39.0 kcal mol$^{-1}$ which becomes favorable when electron-donating substituents are present on silicon. This latter path is unprecedented for the analogous isomerization of bicyclo[1.1.0]butane.

Cartesian coordinates and energies of all stationary points are available in the electronic supplementary material.

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