PERKIN 2

Formation of selenaphosphole isomers from 1,2,4-selenadiphosphole by cycloaddition reaction. A synthetic and *ab initio* quantum chemical study

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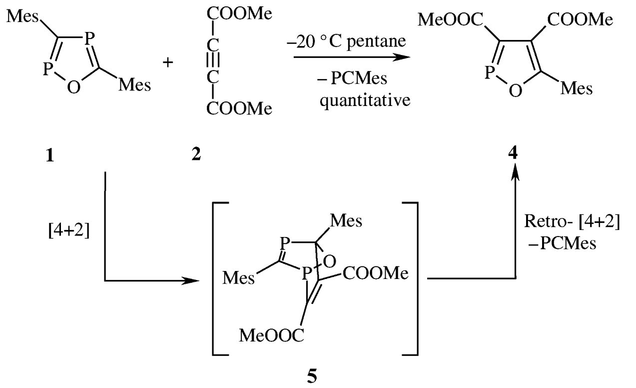
Received (in Cambridge, UK) 24th April 2001, Accepted 13th July 2001
First published as an Advance Article on the web 22nd August 2001

The reaction of 1,2,4-selenadiphosphole with dimethyl acetylenedicarboxylate resulted in a mixture of 1,2-selenaphosphole and 1,3-selenaphosphole at 110 °C in boiling toluene. The mechanism has been interpreted by quantum chemical calculations. A cycloreversion process of the 1,2,4-selenadiphosphole has been ruled out on the basis of the high energy of the selenaphosphirene intermediate. A [4 + 2] cycloaddition of the acetylene on the selenadiphosphole results in the 1,2-selenaphosphole *via* an intermediate. A [3 + 2] cycloaddition *via* a single transition structure results in the 1,3-selenaphosphole. While the energies of the products differ considerably, transition structures on the two cycloaddition routes are predicted to have similar energies, explaining the observed 1 : 1 product ratio.

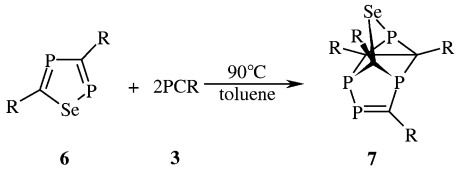
Introduction

Research on phospholes with additional heteroatoms is a field of ongoing interest in the chemistry of low-coordinated phosphorus, as is reflected in several papers and review articles.[1–3] In this paper we continue[3–5] our research on chalcogenadiphospholes,[5] focusing on their reactivity in cycloaddition reactions. As we reported recently,[4] the reaction of the 1,2,4-oxadiphosphole **1** with dimethyl acetylenedicarboxylate (**2**) furnishes 1,2-oxaphosphole **4** readily in quantitative yield under mild reaction conditions (Scheme 1).[4] Tentatively, we assumed the formation of **4** proceeded through a [4 + 2]/retro-[4 + 2] cycloaddition sequence, *via* an oxaphosphanorbornadiene intermediate **5**.



Scheme 1

The potential of selenadiphospholes **6** (which are efficiently available now)[5] to act as a diene in Diels–Alder reactions has already been established. On reacting **6** with **3** a polycyclic structure **7** forms (Scheme 2), as a result of a sequence of cycloaddition reactions.[5] Considering this and the reactivity of oxadiphosphole as mentioned above, in the reaction of **6a** with **2** the formation of 1,2-selenaphosphole **8** was expected.



R: *t*Bu, *t*Pen, 1-Ad

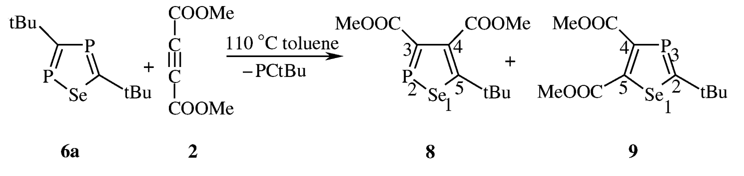
Scheme 2

Herein we report that in the reaction of **6a** with **2** not only the expected **8**, but also the isomeric **9** is formed in a ratio of 1 : 1 (Scheme 3). This observation prompted us to investigate the reaction mechanism by computational means.

Results and discussion

Synthesis of the selenaphospholes 8 and 9

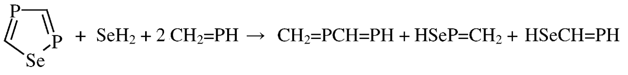
Selenadiphosphole **6a** reacts with acetylene **2** at 110 °C in toluene. The analogous oxadiphosphole **1** reacted, however, readily at −20 °C in pentane.[4] The difference in the substituent pattern (mesityl *vs.* *tert*-butyl) is likely to result in an opposite



Scheme 3

DOI: 10.1039/b103672f

trend, since the larger steric bulk of the mesityl group (on the oxadiphosphole) should reduce the reactivity. The relative inertness of the selenadiphosphole is in accordance with the different aromaticities of the two heterocycles. The HF/6-311+G**//B3LYP/6-311+G** NICS(0) aromaticities[6] are −11.0[7] and −12.7 for **1** and **6** (both with H substituents), respectively. Stabilization energies in semihomodesmotic reactions (for selenadiphosphole see Scheme 4) have been found



$C_2H_2P_2Se + SeH_2 + 2\,CH_2{=}PH \rightarrow CH_2{=}PCH{=}PH + HSeP{=}CH_2 + HSeCH{=}PH$

Scheme 4

to be similar for thiophene and selenophene and also for thiaphospholes (thiadiphospholes) and the corresponding selenaphospholes (selenadiphospholes).[8] Furan and oxaphospholes, however, have considerably smaller stabilization energies in semihomodesmotic reactions than the corresponding sulfur analogues.[9]

The concomitant formation of the *tert*-butylphosphaacetylene **3b** with the products (**8** and **9**) was monitored by NMR spectroscopy. The resulting mixture of the two selenaphospholes **8** and **9** can easily be separated in 40% yield, by multiple application of distillative and chromatographic methods. This procedure, however, causes a strong decrease in the yield. The elemental composition of the isomers was confirmed by their high resolution mass spectra and the characteristic isotope pattern of the molecular ion peak, for both a mixture of **8** and **9** and each of the isolated compounds. The ^{31}P NMR data already elucidate the structures of the products: for each isomer a singlet in the low-field region typical of heterophosphole systems with σ^2,λ^3-phosphorus (δ = 256.5 and 224.4, for **8** and **9**, respectively) is detected. Both signals exhibit selenium satellites, a $^1J_{P,Se}$ coupling of 444 Hz in the case of the lower field signal and a $^2J_{P,Se}$ coupling of 51 Hz in the case of the higher field signal respectively. The elimination of the phosphaalkyne subunit from the selenadiphosphole **6a** is also indicated by the ^{1}H NMR spectra. Each spectrum of **8** and **9** reveals only one *tert*-butyl group at δ = 1.21 (singlet, **8**) and δ = 1.13 (doublet, $^4J_{P,H}$ = 1.23 Hz, **9**) respectively according to the integral ratio to the two methyl groups of the ester moieties.

Mechanistic aspects

To investigate the possible mechanism of the reaction, first all substituents were replaced by hydrogens. The effect of the *t*Bu and the COOMe groups will also be considered and the influence of these substituents on the reaction will be discussed.

The products (C_3H_3PSe and HCP) are lower in energy than the reactants ($C_2H_2P_2Se$ and C_2H_2). The 1,2-selenaphosphole is more stable than the 1,3 isomer by as much as 20 kcal mol^{-1} (B3LYP/6-311+G**). The steric repulsion of the substituents modifies this energy difference; dimethyl 5-*tert*-butyl-1,2-selenaphosphole-3,4-dicarboxylate is by 12.4 kcal mol^{-1} more stable than dimethyl 2-*tert*-butyl-1,3-selenaphosphole-4,5-dicarboxylate (at the B3LYP/6-31+G* level). Since this large energy difference would result in a single product, the reaction should be controlled by kinetic, rather than thermodynamic, factors. Thus we have located the transition structures in the course of the reaction.

To account for the formation of the 1,3-selenaphosphole, first we considered a cycloreversion process of the 1,2,4-selenadiphosphole, leading to a 1,3-dipole (**10**) and phosphaacetylene (Scheme 5). (It should be noted that an analogous intermediate with sulfur instead of Se was first postulated by Märkl.)[10] **10** (R: H) — similarly to its sulfur analogue[11] — could not be located on the potential energy hypersurface. Selenaphosphirene **11**, however, turned out to be a stable

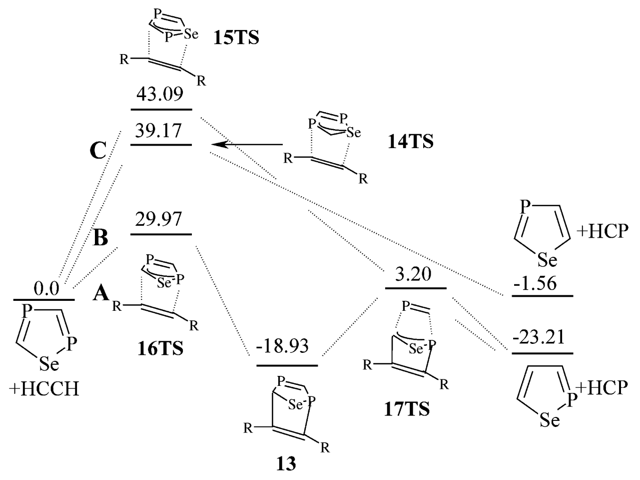
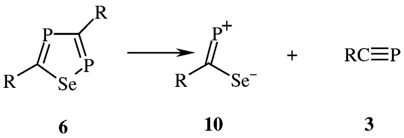
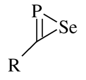


Fig. 1 B3LYP/6-311+G** relative energies of the educts, transition structures, intermediates and products in the $C_2H_2P_2Se + C_2H_2$ reaction in kcal mol^{-1}.

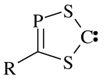


Scheme 5

minimum,[12] which could possibly react with **2** to form either **8** or **9**. Since **11** (R: H) + HCP is higher in energy than 1,2,4-selenadiphosphole by 72.4 kcal mol$^-$, the present reaction is unlikely to proceed *via* this intermediate. It is worth noting that a similar conclusion has recently been drawn on investigating the reaction CS_2 + RCP, where the analogous thiophosphirene fragment (which could have been obtained by cycloreversion from the 1,3,4-dithiaphosphol-2-ylidene intermediate **12**) was also of high energy.[11]



11



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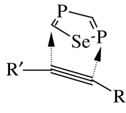
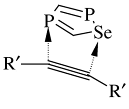
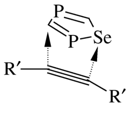
Thus, the reaction should proceed without the prior decomposition of the five-membered ring. Since both of the products (**8** and **9**) contain selenium, three possibilities (**A**–**C**) are conceivable for the acetylene attack.



A



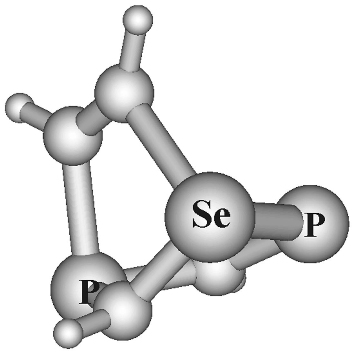
B



C

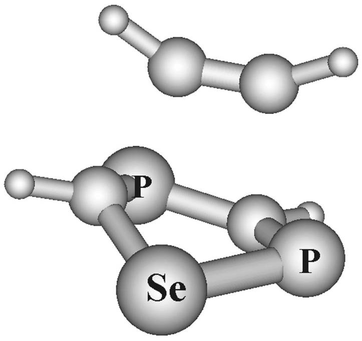
The [4 + 2] cycloaddition — similarly to the reaction considered for the 1,2,4-oxadiphosphole previously[4] — is of **A** type, and is likely to proceed *via* an intermediate (*cf.* Scheme 1), resulting in 1,2-selenaphosphole (**8**). From **B**, the 1,3-selenaphosphole (**9**) can be obtained, while a **C** type attack results again in a 1,2-selenaphosphole (**8**). If the substituents attached to the carbons are different groups, the 1,2-selenaphosphole obtained by an **A** type attack is an isomer of that obtainable by the **C** type attack. Experimentally, only 1,2-selenaphosphole has been observed, which is the result of an **A** type attack.

Optimizing the possible intermediates (of **A**, **B** and **C** type), only the **A** type structure (**13** — see Fig. 1) turned out to be a



14TS

Fig. 2 B3LYP/6-311+G** optimized structures of the unsubstituted **14TS** as plotted by the MOLDEN program.[16]



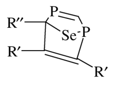
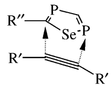
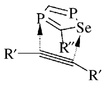
16TS

Fig. 3 B3LYP/6-311+G** optimized structure of **16TS** as plotted by the MOLDEN program.[16]

minimum. The **B** and **C** type structures (**14TS** and **15TS**) — none of them can be described by a conventional valence formula without charge separation[13] — are first order saddle points.[14] Intrinsic reaction coordinate (IRC) calculations confirm that **14TS** (Fig. 2) and **15TS** are located on the reaction path connecting the separated educts (acetylene and 1,2,4-selenadiphosphole), and the products HCP and 1,3- as well as 1,2-selenaphosphole, respectively. For the **A** type reaction, two transition structures [**16TS** (Fig. 3) and **17TS**] connecting **13** with the educts and the products, respectively, could also be located. The relative energies of the minima and transition structures found on the reaction path are shown in Fig. 1.

The lowest energy path is the [4 + 2] cycloaddition, leading to the 1,2-selenaphosphole. The highest energy point in this path is **16TS** (by 30 kcal mol^{-1} above the reactants), which is the transition structure of the cycloaddition step. It is worth noting that for the 1,2,4-oxadiphosphole + acetylene reaction a transition structure similar to **16TS** (by only 19.7 kcal mol^{-1} above the reactants) and an intermediate similar to **13** have been obtained, in accordance with the previously surmised[4] reaction mechanism (see Scheme 1). The observation that the transition structure for the oxadiphosphole + acetylene reaction is by about 10 kcal mol^{-1} lower than for the selenadiphosphole analogue is in agreement with the observed mild reaction conditions in the case of the oxadiphosphole (see Introduction). The relative heights of the calculated reaction barriers are in accordance with the calculated NICS aromaticities. Intermediate **13** is lower in energy than the reactants. The **B** type reaction path has a transition state (**14TS**), which is higher in energy by 9.2 kcal mol^{-1} than the highest energy point for the [4 + 2] cycloaddition (**16TS**). Reoptimization of **13**, **14TS** and **16TS** at the MP2/6-31G* level of the theory resulted in relative energy differences which are similar to the results

Table 1 Effect of the R′ groups and the H–*t*Bu replacement at the carbon α to Se on the relative energies of the transition structures **14TS** and **16TS** to the intermediate (**13**) in kcal mol^{-1}, as calculated at the B3LYP/6-31+G* level. MP2/6-31G*//B3LYP/6-31+G* for R′: COOH and R″: *t*Bu, as well as MP2/6-31G*//MP2/6-31G* data for R′ = R″: H are in parentheses

	 **13**	 **16TS**	 **14TS**
R′: H; R″: H	0.0	48.9 (49.6)	58.1 (60.4)
R′: COOH; R″: *t*Bu	0.0	45.1	53.0
R′: H; R″: *t*Bu	0.0	46.7	54.6
R′: COOH; R″: *t*Bu	0.0	40.6 (47.5)	46.4 (48.0)

obtained from the density functional level calculations (see Table 1). The third pathway of a **C** type attack is of highest energy among the three possibilities. The high energy of this pathway is in accordance with the fact that no dimethyl 3-*tert*-butyl-1,2-selenaphosphole-4,5-dicarboxylate but only dimethyl 5-*tert*-butyl-1,2-selenaphosphole-3,4-dicarboxylate has been observed in the reaction.

Thus, while the **A** and **B** type reactions give an explanation for the observed products (**8** and **9**), their energy difference (9.2 kcal mol^{-1}) is too large to account for the observed 1 : 1 product ratio. A likely reason for this energy difference is the neglect of the substituent effects.

First we take the effect of the carboxy group into consideration, substituting the acetylene with COOH groups. The energy difference between the highest energy transition structure on path **A**, and path **B** decreases to 7.9 kcal mol^{-1}, which is still too large to account for the observed product ratio. The energy of the **C** route[14] is by 8.1 kcal mol^{-1} higher than that of the **B** route with this substituent.

Our second choice was to consider the effect of the *t*Bu group. Due to the steric bulk of this group, the **A** and **C** routes should be more destabilized by the *t*Bu substituent, since in these cases the carbon and not the phosphorus atoms are approached by the attacking acetylene (see Fig. 2). While the **C** route is of high energy, and the corresponding product has not been obtained, we focus on the **A** and **B** routes. For reasons of economy we investigate the effect of the sterically demanding *t*Bu substituent in the α-position from the Se atom only. At the B3LYP/6-31+G* level, the highest point of the **A** reaction path is by 7.9 kcal mol^{-1} lower than the transition structure on the **B** path. Combining the effect of the substituents (with COOH groups on acetylene, and *t*Bu groups at the α-position from the selenium) the energy difference of the **A** and **B** reaction paths reduces to 5.7 kcal mol^{-1} at the B3LYP/6-31+G* level of the theory. The relative energies of **14TS** and **16TS** with respect to **13** are collected in Table 1, showing that the steric bulk of the substituents reduces the energy difference between the **A** and **B** reaction paths. Further calculations were carried out at the MP2/6–31G*//B3LYP/6-31+G* level, to estimate the effect of the method used. These results predict that **14TS** is by only 0.5 kcal mol^{-1} higher in energy than **16TS** with substituents COOH and *t*Bu groups, and this small energy difference is in much better agreement with the 1 : 1 product ratio observed than the density functional results. Since the MP2 relative energies are close to the B3LYP results in the parent molecules (see Table 1), while differing significantly in the case of the substituted systems (with the COOH and tBu substituents) — in agreement with the experimental results — we conclude that at the MP2 level the substituent effects (most likely the steric repulsion) are more properly described than by the present density functional calculations. This behaviour is in accordance with the known shortcomings of the density functional calculations in describing weak long range interactions (*e.g.* van der Waals complexes). Such interactions obviously have a considerable effect, when the steric repulsion of the *tert*-butyl groups should be taken into consideration.

Experimental

General

The reaction and all purification steps were carried out under argon (purity > 99.998%) in previously baked-out and evacuated apparatus (Schlenk techniques). The solvents were dried by standard procedures, distilled, and stored under argon prior to use. Mass spectra: Finnigan MAT 90 spectrometer. NMR spectra: Bruker AMX 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz) and Bruker AC 200 (^{31}P: 81 MHz) spectrometers, solvent as internal standard (^{1}H and ^{13}C); the chemical shifts for ^{31}P NMR are relative to external 85% orthophosphoric acid. The selenadiphosphole **6a** was prepared according to a reported method.[5]

Synthesis of the selenaphospholes 8 and 9

160 mg (0.57 mmol) of 1,2,4-selenadiphosphole **6a** were heated with an excess of dimethyl acetylenedicarboxylate (**2**, 105 µL, 0.86 mmol) for 5 days in toluene (4 mL) in a Schlenk pressure tube at 110 °C. The ^{31}P NMR reaction monitoring indicated the formation of the selenaphospholes **8** and **9**. *tert*-Butylphosphaacetylene **3b** was also formed together with some decomposition products.

Bulb-to-bulb distillation at 150 °C/2 × 10^{-3} mbar furnishes a pure mixture of **8** and **9** in a 1 : 1 ratio. The yield of the mixture is 74 mg (0.23 mmol, 40%), sufficient for recording the ^{13}C NMR spectra. Multiple bulb-to-bulb distillation and subsequent column chromatography (silica gel, pentane–ether = 25 : 1) provide complete separation of the selenaphospholes **8** and **9** in 3% and 5% yield respectively.

Dimethyl 5-*tert*-butyl-1,2-selenaphosphole-3,4-dicarboxylate (8). Yield 5.5 mg (0.02 mmol, 3%) as a yellowish oil (bp: 140 °C/2 × 10^{-3} mbar); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 256.5$ (s, $^1J_{Se,P} =$ 444 Hz); ^{1}H NMR (C_6D_6). $\delta = 1.21$ (s, 9H, $C(CH_3)_3$), 3.24 (s, 3H, CO_2CH_3), 3.58 (s, 3H, CO_2CH_3); MS (EI, 70 eV): *m*/*z* (%): 322 (69) [M^+], 307 (34) [$M^+ - CH_3$], 291 (21) [$M^+ - OMe$], 275 (29) [$M^+ - OMe - O$], 111 (26) [SeP^+], 93 (100) [$SeCH_2^+$], 69 (25) [C*t*Bu^+], 57 (36) [*t*Bu^+], 41 (55) [$C_3H_5^+$]; HR MS (EI): calcd. 322.0060, found 322.0061.

Dimethyl 2-*tert*-butyl-1,3-selenaphosphole-4,5-dicarboxylate (9). Yield 9.3 mg (0.03 mmol, 5%) as a pale yellow oil (bp: 155 °C/2 × 10^{-3} mbar); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 224.4$ (s, $^2J_{Se,P} = 51$ Hz); ^{1}H NMR (C_6D_6): $\delta = 1.13$ (d, 9H, $^4J_{P,H} = 1.23$ Hz, $C(CH_3)_3$), 3.28 (s, 3H, CO_2CH_3), 3.48 (s, 3H, CO_2CH_3); MS (EI, 70 eV): *m*/*z* (%): 322 (61) [M^+], 307 (44) [$M^+ - CH_3$], 291 (29) [$M^+ - OMe$], 275 (41) [$M^+ - OMe - O$], 99 (83) [$M^+ -$ PC*t*Bu − SeH], 93 (100) [$SeCH_2^+$], 69 (26) [C*t*Bu^+], 57 (26) [*t*Bu^+], 41 (67) [$C_3H_5^+$]; HR MS: calcd. 322.0060, found 322.0058.

^{13}C{^{1}H} NMR (C_6D_6) [mixture of two isomers]: $\delta = 35.4$ (s, $C(CH_3)_3$), 35.9 (d, $^3J_{P,C} = 2.6$ Hz, $C(CH_3)_3$), 40.7 (d, $^3J_{P,C} = 5.1$ Hz, $C(CH_3)_3$), 43.5 (d, $^2J_{P,C} = 16.0$ Hz, $C(CH_3)_3$), 51.9 (s, OCH_3), 52.5 (s, OCH_3), 52.5 (s, OCH_3), 52.7 (s, OCH_3), 160.0 (s, C=O), 160.2 (d, $^2J_{P,C} = 10.1$ Hz, C=O), 162.2 (d, $^2J_{P,C} = 2.6$ Hz, *ring*-C), 164.2 (s, C=O), 164.9 (d, $^2J_{P,C} = 10.1$ Hz, C=O), 167.4 (d, $^1J_{P,C} = 81.4$ Hz, *ring*-C), 167.5 (d, $^1J_{P,C} = 118.7$ Hz, *ring*-C), 168.5 (d, $^2J_{P,C} = 2.5$ Hz, *ring*-C), 177.8 (d, $^2J_{P,C} = 7.6$ Hz, *ring*-C), 210.2 (d, $^1J_{P,C} = 69.5$ Hz, *ring*-C).

Calculations

The calculations were carried out by using the GAUSSIAN 98 package.[15] Geometries were fully optimized at the B3LYP-6-311+G** level of the density functional theory. At the stationary points second derivatives were calculated, showing whether a minimum or a first order saddle point was obtained. Subsequent IRC (intrinsic reaction coordinate) runs at the transition structures have shown those minima which are connected by the transition structure. For the structures with COOH and *t*Bu substituents the calculations were carried out at the B3LYP/6-31+G* level of the theory. Single point MP2/6-31G*//B3LYP/6-31+G* calculations have also been carried out for the largest systems studied. For the substituted cases MP2/6-31G* calculations were carried out too. Calculation of the Gibbs free energies of the transition structures and intermediates revealed that there is little change in comparison to the relative energies of these structures.

Acknowledgements

We are grateful to the *Deutsche Forschungsgemeinschaft* (Graduate College *Phosphorus as Connecting Link between Various Chemical Disciplines*) for generous financial support and to the *Volkswagen-Stiftung* as well as OTKA T026335. The generous allocation of computer time from Regionales Hochschules Rechnerzentrum Kaiserslautern is also gratefully acknowledged.

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14 It should be noted that, contrary to the results obtained with hydrogens on the carbons, whereby a single transition state has been obtained on the **C** reaction path—see Fig. 1, substituting the β carbon atom by a *t*Bu group results in an additional intermediate and thus a second transition structure on this reaction channel. The **C** path remains the highest energy one with the *t*Bu substituent too.

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