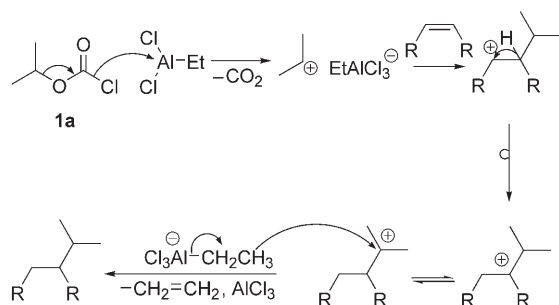


Intramolecular Concerted Insertion of Vinyl Cations into C–H Bonds: Hydroalkylating Cyclization of Alkynes with Alkyl Chloroformates To Give Cyclopentanes**

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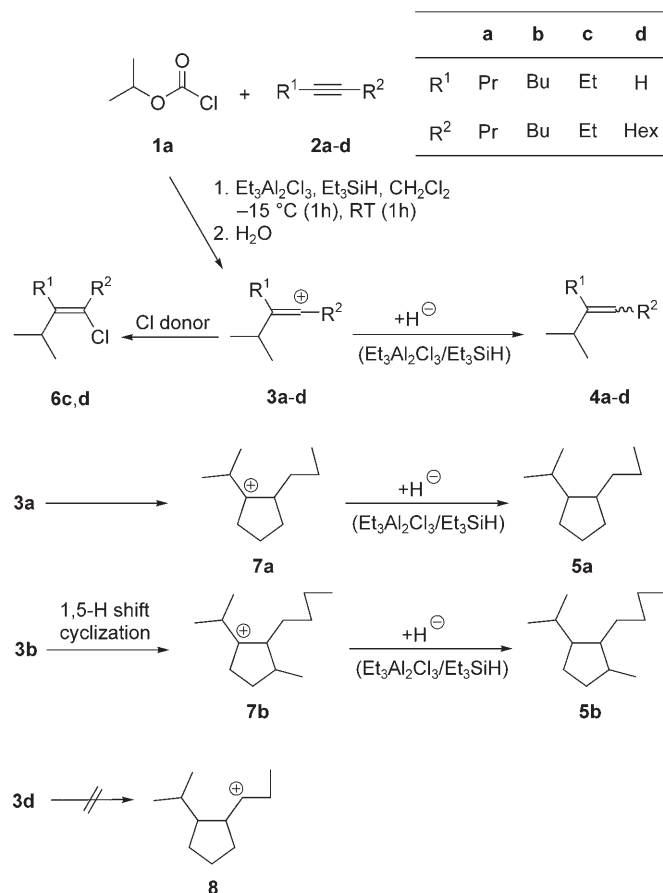
C–H insertions with formation of a new C–C bond are of topical interest.^[1] At present, great efforts are devoted to developing the transition-metal-catalyzed C–H insertion.^[2] The insertion of carbenes into C–H bonds proceeds by direct attack of a nonactivated C_{sp}³–H bond and formation of a new C–C bond in a concerted one-step reaction.^[3] Theoretical studies^[4,5] as well as experimental investigations in the gas phase^[6] have shown that the vinyl cation C₂H₃⁺ can insert into the H–H bond by formation of the ethyl cation^[4,6] and into the C–H bond of methane and of ethane by formation of the 2-propyl cation^[6] and the 2-butyl cation,^[5] respectively.

Recently we reported on the hydroalkylation of alkenes with alkyl chloroformates induced by ethylaluminum sesquichloride (Et₃Al₂Cl₃).^[7] The reaction of the Lewis acid, for example, with isopropyl chloroformate (**1a**) gives the isopropyl cation, which adds across the alkene. Transfer of a hydride ion from an ethylaluminum sesquichloride species to the adduct carbenium ion takes place by formation of the hydroalkylation product (Scheme 1).



Scheme 1. Mechanism of the hydroalkylation of alkenes with isopropyl chloroformate (**1a**) induced by ethylaluminum sesquichloride. R = alkyl.

The application of this reaction to alkynes was expected to give analogously alkylated alkenes. The reaction of 4-octyne (**2a**) and **1a** under similar reaction conditions in the presence of Et₃Al₂Cl₃ and with Et₃SiH as an additional hydride donor^[8] was expected to proceed via vinyl cation **3a** to give 4-isopropyl-4-octene (**4a**) (Scheme 2). To our surprise this



Scheme 2. Reactions of alkynes **2a–d** with **1a** in the presence of Et₃Al₂Cl₃/Et₃SiH proceeding via vinyl cations **3a–d**. Products **5a,b** and **6c,d** as well as the side products **4a–d** were obtained as mixtures of diastereomers. Products derived from the exocyclic cyclopentyl cation **8** were not observed.

product was formed only as a side product (<5%). We isolated 1-isopropyl-2-propylcyclopentane (**5a**) in 79% yield as a mixture of two diastereomers in a ratio of 4.6:1. The analogous reaction of 5-decyne (**2b**) afforded the 1,2,3-trialkyl-substituted cyclopentane **5b** in 74% yield as a mixture of four diastereomers in a ratio of 11:6:1:1. In this case, too, the hydroalkylation product **4b** was formed in only trace amounts (<2%). The analogous reaction of 3-hexyne (**2c**) gave chloroalkene **6c** as a diastereomeric mixture (1.3:1) in 38% yield. The hydroalkylation product **4c** was obtained in about 12% yield. Reaction of 1-octyne (**2d**) with **1a** in the presence of Et₃Al₂Cl₃ afforded the chloroalkylation product **6d** in 40% yield as a diastereomeric mixture and about 5% of the hydroalkylation product **4d**. A cyclopentane derivative or another cyclic product was not observed in either reaction.

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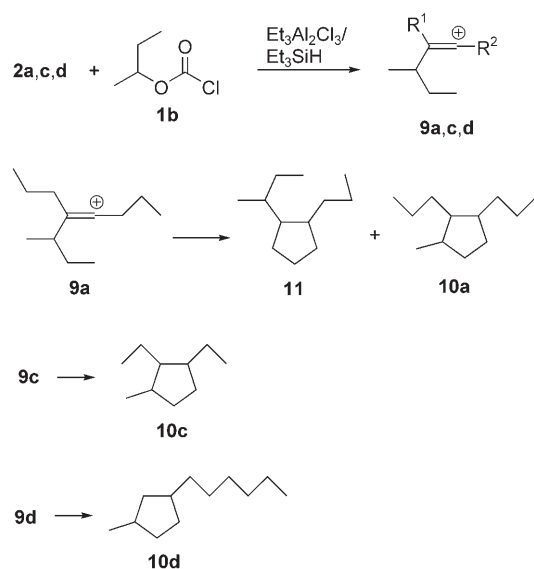
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The formation of products **4–6** can be explained as follows: The initially formed 2-propyl cation adds across the C–C triple bond to give vinyl cations **3**. If a C–H bond is available in position 5 of **3** an intramolecular 1,5-hydride shift takes place to give cyclopentyl cations **7a** and **7b**, respectively, with formation of a new C–C bond. Finally, intermolecular hydride transfer leads to the products **5a** and **5b**, respectively.^[9] The intramolecular 1,5-hydride shift is definitely faster than the intermolecular hydride transfer from Et₃Al₂Cl₃ or Et₃SiH yielding hydroalkylation products **4**. In the case of alkyne **2c** a 1,5-hydride shift is not possible. Therefore vinyl cation **3c** is mainly trapped by transfer of a chloride ion from chloroformate **1a** or an EtAlCl₃[–] species to give chloroalkenes **6c**. Apparently the transfer of a chloride ion to the vinyl cation intermediate is faster than the transfer of a hydride ion. Marcuzzi and Melloni reported on the chloroalkylation of alkynes using chloroalkanes in the presence of Lewis acids.^[10]

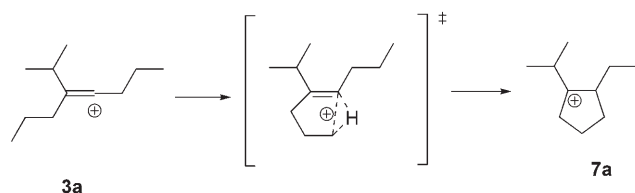
In analogy, the cyclization of vinyl cation **3d** should be possible by formation of the exocyclic carbenium ion **8**. However, products derived from **8** were not observed, giving evidence that a fast 1,5-hydride shift takes place only if an endocyclic carbenium ion such as **7a,b** is formed. Thus, alkynes **2c** and **2d** were treated with 2-butyl chloroformate (**1b**) in the presence of Et₃Al₂Cl₃ and Et₃SiH. As expected, we observed the formation of the cyclopentane derivatives **10c** and **10d** via vinyl cations **9c** and **9d**, respectively (Scheme 3). The diastereomeric mixtures of compounds **10c** and **10d** were obtained in yields of 26 % (GC) and 13 % (GC), respectively. Interestingly, the reaction of alkyne **2a** with alkyl chloroformate **1b** via vinyl cation **9a** gave cyclopentane **10a** as well as **11** (total yield: 52 %) in a ratio of 1:3.

There are some questions concerning the mechanism of the formation of the cyclopentanes. Schegolev et al. reported



Scheme 3. Reaction of alkynes **2a,c,d** with **1b** in the presence of Et₃Al₂Cl₃/Et₃SiH proceeding via vinyl cations **9a,c,d** to give the products of a hydroalkylating cyclization **10a,c,d** and **11**. Cyclopentanes **10a** and **11** are formed in a ratio of 1:3 via vinyl cation **9a**. The cyclopentanes were obtained as mixtures of diastereomers. For R¹, R², see Scheme 2.

on the formation of cyclopentenone derivatives by additions of acyl cations to alkynes. They discussed a 1,5-hydride shift of the initially formed acyl vinyl cation followed by an addition–elimination reaction A_DE or alternatively an intramolecular electrophilic substitution S_Ei.^[11] In our case both mechanistic alternatives can be excluded with certainty. Cyclopentene derivatives formed as products of a S_Ei reaction were not observed even in trace amounts. The alternative 1,5-hydride transfer followed by an addition reaction to give a cyclopentyl cation, which under our reaction conditions could be trapped by a hydride donor, can be excluded, too, because in this case the vinyl cation intermediates **3a** and **3b** should give initially a primary and secondary alkyl carbenium ion, respectively. Our investigations of hydroalkylations of alkenes have shown that 1,2-H shifts of the alkyl carbenium ion intermediates are always faster than all kinds of possible inter- and intramolecular trapping reactions.^[7] However, products of these rearranged carbenium ions, such as cyclobutanes, were not observed. Thus, the 1,5-H shift and the cyclization must proceed in a concerted reaction (Scheme 4).



Scheme 4. Concerted intramolecular insertion of vinyl cation **3a** into a primary C–H bond to give the cyclopentyl carbenium ion **7a**.

Our quantum-mechanical calculations (MP2/6-311 + G-(d,p)//MP2/6-31G(d) + ZPVE)^[12] predict that this concerted insertion of vinyl cation **3a** into a C–H bond is a possible pathway. After the exothermic formation of **3a** (–197 kJ mol^{–1}), the reaction proceeds via the transition state of the concerted process (Figure 1), leading directly to the cyclopentyl cation **7a**. While the latter is stabilized by about 130 kJ mol^{–1} relative to **3a**, the activation energy for the cyclization and simultaneous hydrogen transfer is only 8 kJ mol^{–1}. The formation of a primary alkyl carbenium ion by 1,5-hydride shift followed by C–C bond formation can be ruled out because the carbenium ion is not a minimum on the potential energy surface but rearranges by a 1,2-hydrogen shift to give a secondary alkyl carbenium ion, which cannot form cyclopentanes. Analysis of the transition state's single imaginary frequency reveals a motion of the bond-forming carbon atoms towards each other, while the hydrogen atom is moving above the ring system. The relevant distances are in accordance with those of an insertion of the ethenyl cation into the C–H bond of ethane^[5] and those of comparable C–H insertion reactions of carbenes.^[13–15]

Surprisingly, vinyl cation **3d** does not form an exocyclic secondary cyclopentyl cation **8**. The reason could be that the generation of a secondary cation is energetically less favorable than formation of a tertiary endocyclic carbenium ion. Our calculations with the model vinyl cation **3e** (R¹ = Pr, R² = Bu) demonstrate that the formation of the exocyclic carbenium ion **12** is in particular kinetically disfavored (Scheme 5).

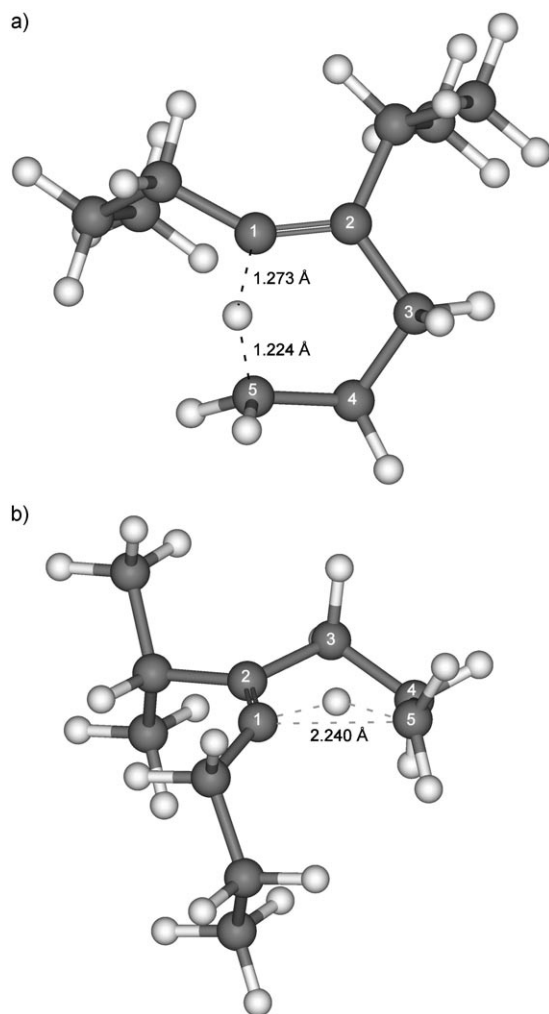
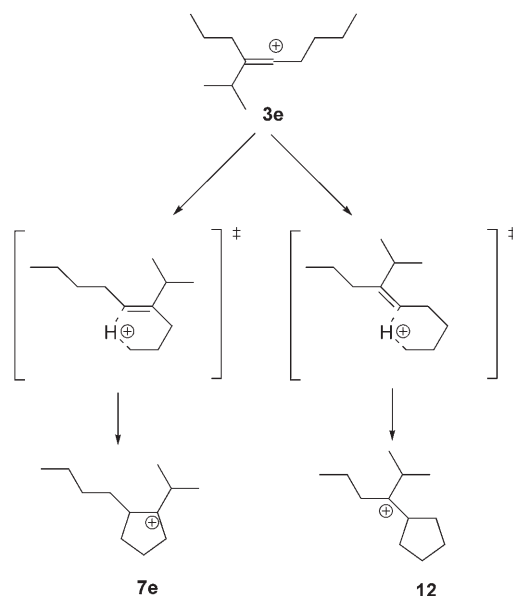


Figure 1. Transition state for the concerted formation of cyclopentyl cation **7a** from vinyl cation **3a**. Relevant C–H and C–C distances are given. a) View of the forming cyclopentane ring in the plane. b) The view of the forming cyclopentane ring perpendicular to the plane reveals a boatlike orientation; carbon atoms 2–4 lie above the C1–H–C5 plane. The C1–H–C5 angle is 127.5°.

While the cyclopentyl cation **7e** as the *endo* product is as stable as the corresponding *exo* product **12**, there is a significant difference in the transition states. The formation of the exocyclic carbenium ion **12** is no longer a concerted process, but its transition state corresponds more to a hydride transfer transition state.^[16] Its barrier is calculated to be about 20 kJ mol^{−1} higher in energy than that for the formation of the observed endocyclic cation **7e**.

Our experimental results and the quantum mechanical calculations clearly indicate that 1,5-H shift and cyclization of vinyl cations **3a,b** as well as **9a,c,d** should be concerted processes, allowing the preparatively useful intramolecular insertion of a vinyl cation into C–H bonds^[4–6] in solution, in analogy to the insertion of singlet carbenes.^[3,17]

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Scheme 5. Model reaction of vinyl cation **3e** by endo- and exocyclic pathways to give the cyclopentyl cations **7e** and **12**.

Keywords: alkylation · alkynes · C–H insertion · cyclopentanes · vinyl cations

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