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Chiral Propargylic Cations as Intermediates in S_N1-Type Reactions: Substitution Pattern, Nuclear Magnetic Resonance Studies, and Origin of the Diastereoselectivity

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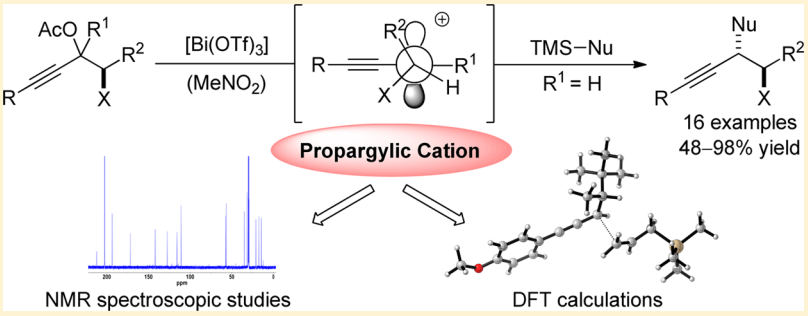
Supporting Information



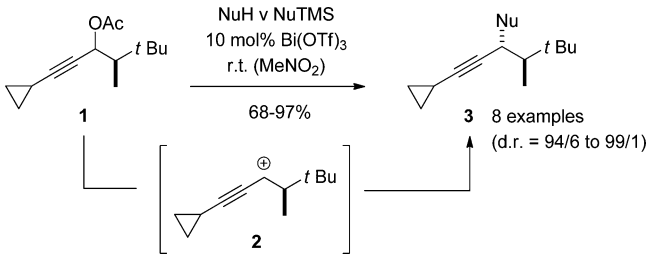
ABSTRACT: Nine propargylic acetates, bearing a stereogenic center (−C*HXR^2) adjacent to the electrophilic carbon atom, were prepared and subjected to S_N1-type substitution reactions with various silyl nucleophiles employing bismuth trifluoromethanesulfonate [Bi(OTf)$_3$] as the Lewis acid. The diastereoselectivity of the reactions was high when the alkyl group R^2 was tertiary (*tert*-butyl), irrespective of the substituent X. Products were formed consistently with a diastereomeric ratio larger than 95:5 in favor of the *anti*-diastereoisomer. If the alkyl substitutent R^2 was secondary, the diastereoselectivity decreased to 80:20. The reaction was shown to proceed stereoconvergently, and the relative product configuration was elucidated. The reaction outcome is explained by invoking a chiral propargylic cation as an intermediate, which is preferentially attacked by the nucleophile from one of its two diastereotopic faces. Density functional theory (DFT) calculations suggest a preferred conformation in which the group R^2 is almost perpendicular to the plane defined by the three substituents at the cationic center, with the nucleophile approaching the electrophilic center opposite to R^2. Transition states calculated for the reaction of allyltrimethylsilane with two representative cations support this hypothesis. Tertiary propargylic cations with a stereogenic center (−C*HXR^2) in the α position were generated by ionization of the respective alcohol precursors with FSO_3H in SO_2ClF at −80 °C. Nuclear magnetic resonance (NMR) spectra were obtained for five cations, and the chemical shifts could be unambiguously assigned. The preferred conformation of the cations as extracted from nuclear Overhauser experiments is in line with the preferred conformation responsible for the reaction of the secondary propargylic cations.

INTRODUCTION

The nucleophilic displacement of an appropriate leaving group by a carbon nucleophile at a propargylic alcohol or its derivative represents a useful synthetic transformation.[1] Despite the progress made in S_N1-type bond formation reactions starting from propargylic alcohols,[2−4] propargylic esters,[5] or propargylic ethers,[6] there is little information about the stereochemical course of this substitution if a stereogenic center resides in the α position to the electrophilic center. Indeed, the limited knowledge on the facial diastereoselectivity of nucleophilic addition reactions at prostereogenic cationic carbon centers[7,8] is striking if compared to the extensive data set that has been accumulated over the years on the addition of strong nucleophiles to chiral aldehydes.[9] We addressed this issue some time ago by studying the reaction of propargylic acetates, which bear a stereogenic 2-(3,3-dimethyl)butyl substituent (−CHMe*t*Bu) at the electrophilic carbon center.[10] It was found that the reaction with aromatic nucleophiles (NuH) and silylated nucleophiles (NuTMS), such as silyl enol ethers and allylsilanes, proceeds with high diastereoselectivity. As an example, the reaction of acetate **1** is shown in Scheme 1. It delivered the respective *anti*-products **3** upon treatment with a nucleophile and with 10 mol % Bi(OTf)$_3$ (Tf = trifluoromethanesulfonyl) in nitromethane as the solvent. The reaction was shown to be stereoconvergent; i.e., the relative

Received: November 21, 2013
Published: February 4, 2014

Scheme 1



configuration of the substrate had no influence on the product configuration, supporting the intermediacy of cation **2** in the reaction course.

To explain the outcome of the reaction, the conformation of cations, such as **2**, was analyzed by density functional theory (DFT) calculations and a local minimum was found, in which a preferred attack from one face was favored. The results were, however, not verified by further calculations on the transition state of the reactions. The scope was limited to substrates with the same propargylic unit and with a single stereogenic substituent. To obtain a more comprehensive picture on the intriguing issue of acylic stereocentrol in carbocation reactions,[11] we have now extended the substrate scope to propargylic acetates of general structure **A** (Figure 1), in which

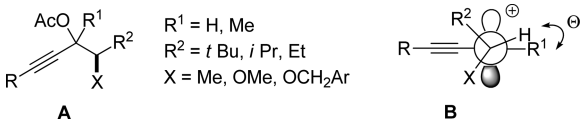


Figure 1. General structure of propargylic acetates **A**, which were employed in this study, and general structure of the cations **B** derived from **A** with the dihedral angle Θ being defined with a positive rotation in the direction $R^1 \rightarrow H$.

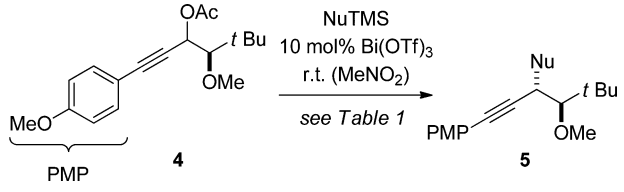
the substituents X and R^2 were varied. Stable carbocations **B** were generated from acetates **A** (R^1 = Me) under superacidic conditions to obtain information on their constitution and conformation in solution. In addition, the transition states of the reaction with an allylsilane as a representative nucleophile were analyzed by DFT calculations. Details of this work are reported in the present account.

RESULTS AND DISCUSSION

Synthetic Studies with Various Substrates of Type A.

In the first set of experiments, nucleophilic substitution reactions were performed with precursors for propargylic carbocations, which bear a methoxy group (X = OMe; Figure 1) at the adjacent stereogenic center. As previously observed (Scheme 1), acetates were superior substrates compared to alcohols, which were not sufficiently reactive, and compared to the very labile mesylates. Acetate **4** (Scheme 2) was obtained by

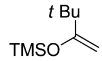
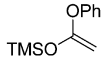
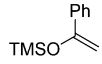
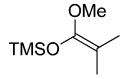
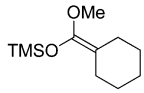
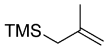
Scheme 2



acetylation of the respective alcohol,[12] which, in turn, was prepared by addition of a PMP-substituted (PMP = *para*-methoxyphenyl) ethynyllithium reagent[13] to 3,3-dimethyl-2-methoxybutanal (see the Supporting Information for further details).[14]

Initial screening was conducted with different Lewis acids, which promote the reaction of acetate **4** with a silyl enol ether.[15] Yields were highest with $Bi(OTf)_3$, which was used as the catalyst throughout this study.[16] The reaction of acetate **4** with various silylated nucleophiles proceeded with high diastereoselectivity and produced *anti*-**5** frequently as the only observed product (Table 1).

Table 1. Diastereoselective Reaction of Propargylic Acetate 4 with Various Silylated Nucleophiles to Products 5

entry[a]	TMS–Nu	product	yield [%][b]	d.r.[c]
1		**5a**	84	> 95:5
2		**5b**	73	> 95:5
3		**5c**	81	> 95:5
4		**5d**	70	> 95:5
5		**5e**	48	> 95:5
6		**5f**	64	87:13
7		**5g**	48	> 95:5

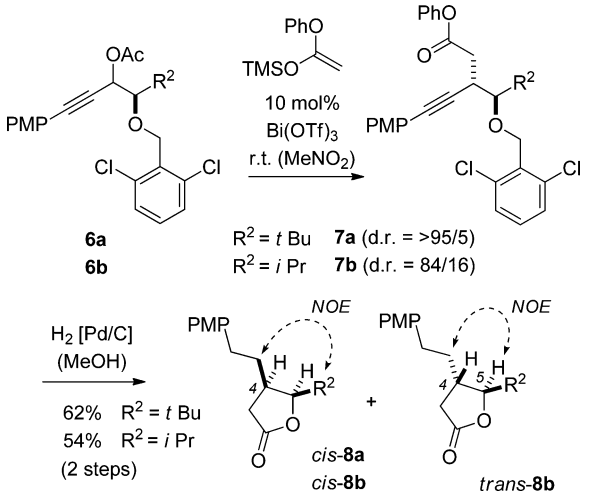
[a]Reactions were performed in deaerated $MeNO_2$ (c = 125 mM) within 30 min (entries 6 and 7) and 60 min (entries 1–5) at ambient temperature. [b]Yield of isolated product after chromatographic purification. [c]The diastereomeric ratio (dr = *anti*/*syn*) was determined by ^{1}H NMR analysis of the crude product mixture.

In the case of product **5a**, it was shown that the product configuration was independent of the relative configuration of the starting material. Irrespective of whether acetate **4** was used as the *anti*-diastereoisomer (dr = 95:5) or as a mixture of diastereoisomers (dr = 58:42), product **5a** was obtained as a single product. The reaction proceeded stereoconvergently, which clearly rules out a S_N2-type displacement. Most silyl enol ethers and silyl ketene acetals reacted smoothly (entries 1–4) and showed no indication of a S_N'-type substitution (i.e., a reaction at the distal position of the propargylic cation). Only with a sterically congested silyl ketene acetal (entry 5), a major side product was observed (see the Supporting Information), which can be explained by an initial S_N' attack. The less reactive allylsilanes (entries 6 and 7) gave slightly lower yields than the silyl enol ethers. Diastereoselectivites were high, however, and could be further improved at low temperatures. When the reaction of entry 6 was performed under otherwise identical conditions at 0 °C, the dr was >95:5 (63% yield).

To chemically ascertain the relative configuration of the propargylic substitution products, the substituent X (Figure 1) was modified (Scheme 3). The 2,6-dichlorobenzyl group was

dx.doi.org/10.1021/ja411772n | J. Am. Chem. Soc. 2014, 136, 2851–2857

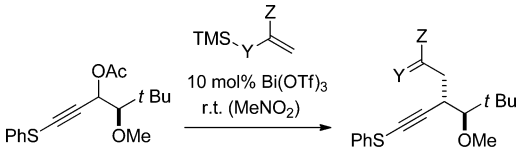
Scheme 3



employed as a cleavable protecting group, which liberates a free hydroxy group upon deprotection. The resulting alcohol, in turn, was expected to close to a γ-lactone ring by a transesterification. The diastereoselectivities in the S_N1-type displacement reaction with the silyl nucleophile remained essentially unchanged for substrate **6a** compared to substrate **4**. The diastereoselectivity for substrate **6b**, bearing an isopropyl group instead of a *tert*-butyl group at the stereogenic center, was lower than that for substrate **6a**, and the formation of a second diastereoisomer was observed. Without purification, products **7** were treated with hydrogen and, as expected, the formation of lactones **8** was observed. Their relative configuration was proven by nuclear Overhauser effect (NOE) studies. In addition, the coupling pattern for the hydrogen atom at C5 in products **8** matched the known coupling pattern of closely related *cis*- and *trans*-substituted γ-lactones.[17] The chemical assignment of the relative configuration was further corroborated for R^2 = *t*-Bu (Figure 1) by crystallographic evidence (see the Supporting Information for further details).

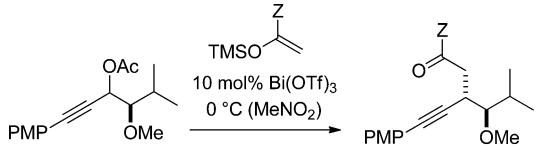
The terminal substituent R (Figure 1) at the propargyl triple bond could be altered from PMP to the synthetically less useful phenyl group. The reactivity of the latter substrate is lower than that of acetate **4**, presumably because of the lower electron-donating property of the phenyl group (see the Supporting Information for further details). A more versatile substituent is the phenylsulfanyl group and the corresponding acetate **9** (Scheme 4) was readily prepared from 3,3-dimethyl-2-methoxybutanal in analogy to substrate **4**.[18] Under $Bi(OTf)_3$ catalysis, allyltrimethylsilane delivered enyne **10a** in good yield and with high diastereoselectivity (dr = 93:7). Substitution by an enolate equivalent was achieved with a silyl enol ether, producing alkynone **10b** as a single diastereoisomer.

Scheme 4



As already seen for substrates **6**, a change of the substituent R^2 (Figure 1) from *tert*-butyl to isopropyl led (while leaving all other parameters constant) to a decrease in diastereoselectivity. When comparing the reactions **4** → **5a** with the reaction **11** → **12a**, a similar chemoselectivity (84% versus 75% yield) but a reduced diastereoselectivity (dr = >95:5 versus 74:26) was recorded at ambient temperature. If the reaction temperature was lowered in the latter case to 0 °C (Scheme 5), the time

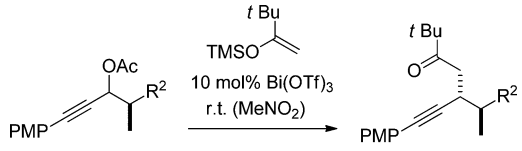
Scheme 5



required to achieve full conversion increased to 4 h (in comparison to 1 h at ambient temperature), with the diastereoselectivity increasing slightly to 79:21. With the silyl ketene acetal derived from phenyl acetate, the respective product **12b** was formed under the same conditions (0 °C and *t* = 4 h) in a yield of 69% and with a diastereomeric ratio of dr = 80:20.

Because the reactions with the α-methoxy group (X = OMe; Figure 1) were mostly performed with a terminal PMP substituent at the alkyne group (substrates **4**, **6**, and **11**), a set of experiments was conducted in which the previously studied[10] −CHM*e*Bu stereogenic unit (Scheme 1) and its R^2 variants (R^2 = *i*-Pr and Et) were probed with propargylic PMP-substituted acetates of type **13** (Scheme 6). The chemical yield

Scheme 6

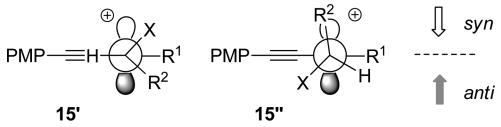


and diastereoselectivity obtained where R^2 = *t*-Bu (product **14a**) was excellent, but while the yields remained high for products **14b** and **14c**, the diastereoselectivity decreased in the order R^2 = *t*-Bu > *i*-Pr > Et.

Mechanistic Considerations and DFT Calculations. From the data accumulated from the synthetic work, it is apparent that a high preference for the formation of the *anti*-product depends upon the presence of a bulky substituent R^2. A decrease in selectivity was observed when this substituent was changed from tertiary (*t*-Bu) to secondary (*i*-Pr), while a primary substituent was poorly selective (Scheme 6). Our studies indicate that there is no electronic influence of the substituent X (X = Me, OMe, and OCH_2Ar), with the reaction outcome not altered if R^2 remains the same. Moreover, the alkynyl substituent (R) also shows no influence on the facial diastereoselectivity observed. In a first approach toward a possible explanation for the selectivity, we studied the conformation of eight different cations **15** with the R

dx.doi.org/10.1021/ja411772n | J. Am. Chem. Soc. 2014, 136, 2851−2857

substituent kept constant (R = PMP) and the substituents X, R^1, and R^2 varied. The DFT calculations were performed with the Gaussian09[19] suite of programs using the B3LYP[20] density functional with the 6-311++G** basis set (similar results were obtained using the M06-2X[21] density functional), scanning the torsion angles at intervals of 15°. As previously found for X = Me, R^1 = H, and R^2 = *t*-Bu,[10] the secondary cations (R^1 = H) show two conformational minima, **15′** and **15″** (Figure 2). For



	15a	15b	15c	15d	15e	15f	15g	15h
R^1	H	H	H	H	Me	Me	Me	Me
R^2	*i* Pr	*t* Bu	*i* Pr	*t* Bu	*i* Pr	*t* Bu	*i* Pr	*t* Bu
X	Me	Me	OMe	OMe	Me	Me	OMe	OMe

Figure 2. Structure and preferred conformation of cations **15** with varying groups R^1 (R = H and Me), R^2 (R = *i*-Pr and *t*-Bu), and X (X = Me and OMe) and direction of attack for *syn*- and *anti*-product formation.

α-alkyl-substituted propargylic cations (X = Me), the dihedral angle Θ (see Figure 1) of the global minimum is close to 180° (**15′**), whereas the second minimum is characterized by a dihedral angle of about 315° (**15″**). In contrast, the global minimum of α-alkoxy-substituted cations (X = OMe) shows a dihedral angle of 315° (**15″**) and a dihedral angle of about 180° for the second relative minimum (**15′**). In all of these cases, the second relative minimum is 0.9−5.3 kJ mol^{-1} higher in energy than the global minimum. For tertiary cations (R^1 = Me), the first conformational minimum shifts to a smaller dihedral angle of about 150°, while the second minimum is observed for a dihedral angle of ca. 340°. The energy difference between the two minima is small (0.6−3.3 kJ mol^{-1}). The conformational analysis of cation **15d** (X = OMe, R^1 = H, and R^2 = *t*-Bu) is shown in Figure 3, while the conformational analyses for the other cations **15a**−**15c** (R^1 = H) and **15e**−**15h** (R^1 = Me) are compiled in the Supporting Information.

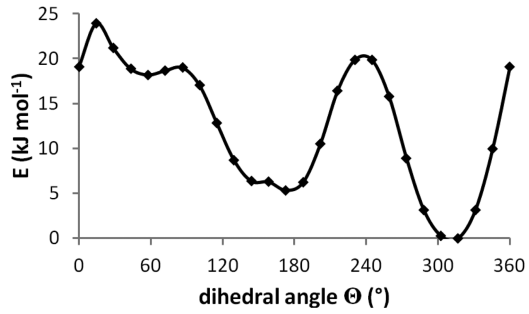


Figure 3. Conformational analysis of cation **15d** (X = OMe, R^1 = H, and R^2 = *t*-Bu) on the basis of DFT calculations (B3LYP 6-311++G**).

In Figure 2, the required direction of nucleophilic attack is indicated for the formation of *syn*- and *anti*-products. The fact that the *anti*-selectivity decreases for R^2 = *t*-Bu > *i*-Pr > Et is difficult to match with a reactive conformation **15′**. In conformation **15″**, however, the group R^2 adopts an almost antiperiplanar orientation to a nucleophile approaching from the bottom side. The direction of the nucleophilic attack correctly explains the experimentally observed *anti*-product and is in line with the size influence at R^2.

To further substantiate the above-mentioned mechanistic picture, DFT calculations were performed, which simulate an approach of allyltrimethylsilane to cations **15b** (X = Me, R^1 = H, and R^2 = *t*-Bu) and **15d** (X = OMe, R^1 = H, and R^2 = *t*-Bu). The corresponding transition states were modeled using the M06-2X[21] density functional and the 6-311++G** basis set, and their nature was confirmed by the presence of one imaginary frequency matching the expected carbon−carbon bond formation. Grimme's D3 dispersion correction,[22] as implemented in Gaussian09,[19] was also employed for the optimization. To test for solvent effects, single-point calculations on the gas-phase-optimized structures were performed with the SMD[23] intrinsic solvation model using the parameters for nitromethane.

In both cases (X = Me and OMe), we found that the transition state **TS″**, in which the nucleophile approaches the cation from the bottom side (Figure 4), was lower in energy than the transition state **TS′**. As a result, the former approach is favored, thus providing an explanation for the experimentally observed *anti*-product.

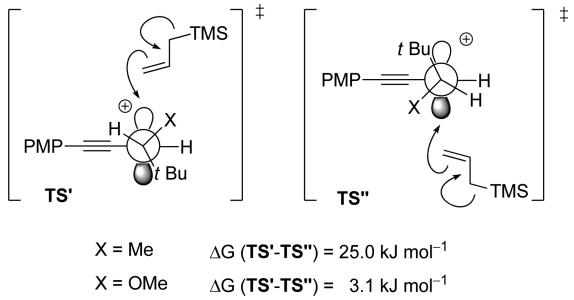


Figure 4. Energy differences between the transition states for the attack of allyl trimethylsilane to cations **15b** (X = Me) and **15d** (X = OMe) from the disfavored (**TS′**) or favored (**TS″**) side, as obtained by DFT calculations (M06-2X-D3 and 6-311+G**).

The structure of the favored transition state **TS″** for the reaction involving **15b** is shown in Figure 5. Structures of all other calculated transition states are provided in the Supporting Information. A prominent difference between the two transition states are the dihedral angles Θ_{attack} formed between the C_{alkyne}−C_{cation} bond of the cation and the double bond of the nucleophile. While the attack of allyltrimethylsilane occurs

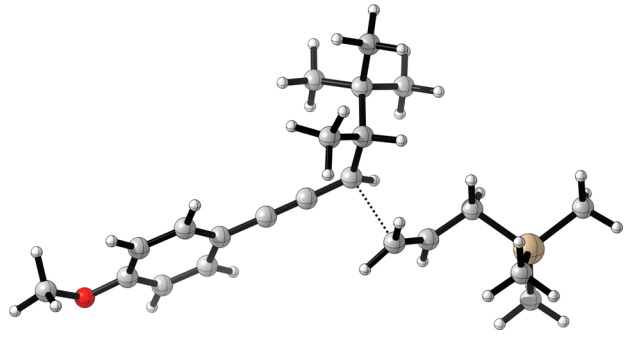


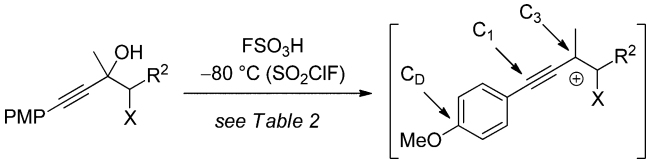
Figure 5. DFT-optimized structures of the preferred transition state **TS″** for the reaction of allyltrimethylsilane and cation **15b**. Red, oxygen; gray, carbon; white, hydrogen; and bronze, silicon. The figure was prepared with CYL view.[24]

dx.doi.org/10.1021/ja411772n | J. Am. Chem. Soc. 2014, 136, 2851−2857

in an almost perpendicular fashion in **TS′** (Θ_{attack} = 95°), this angle is markedly larger for **TS″** (Θ_{attack} = 129°). In contrast, all relevant bond lengths in the cation and the nucleophile are very similar in both transition states. This includes the distance between the carbon atoms of the newly formed bond, which is 2.42 Å for **TS′** and 2.43 Å for **TS″**.

Nuclear Magnetic Resonance (NMR) Spectroscopy Studies. Chiral propargylic cations have not yet been studied in solution, and to our knowledge, there is no information about their constitution or conformation. It seemed therefore appropriate to supplement the synthetic studies and DFT calculations by ^{1}H and ^{13}C NMR spectroscopic investigations of propargylic cations in superacidic solution.[25] Mechanistically, it was interesting to see whether any interactions between the substituent X and the cationic center exist. For X = OMe, for example, the formation of an onium ion was conceivable. Ionization experiments with different superacids (FSO_3H and SbF_5/FSO_3H) were undertaken to find the optimal conditions for the preparation of the carbocations. Unfortunately, it turned out that neither α-alkoxy-substituted nor α-alkyl-substituted secondary (R^1 = H) propargylic alcohols led to stable cations. Instead, a mixture of undefined products was formed under a variety of conditions. To overcome this problem, the corresponding tertiary (R^1 = Me) alcohols were synthesized by simple oxidation of the secondary alcohols and subsequent addition of methyllithium. The synthesis of tertiary alcohols with R^2 = *t*-Bu was not attempted because it is known that the respective cations readily undergo β-elimination with concomitant formation of the *tert*-butyl cation and derived products.[26] Instead, cation precursors were prepared with R^2 = *i*-Pr, Et, and X varied to be methyl, methoxy, and 2,6-dichlorophenylmethoxy ($OBnCl_2$). Treatment of the tertiary alcohols with FSO_3H in SO_2ClF at −80 °C quantitatively generated the cations **15e**, **15g**, **15i**, **15j**, and **15k** (Scheme 7 and Table 2).

Scheme 7



15e, **15g**, **15i**, **15j**, **15k**

The weakly yellow solutions of the cation precursors turned into deep red (**15e**, **15j**, and **15k**), deep yellow (**15g**), and deep brown (**15i**) solutions in the acidic solvent.

Storing these carbocations under superacidic conditions in SO_2ClF at −30 °C for several days and cooling them back to −80 °C did not lead to significant decomposition or side product formation, indicating the high stability of these intermediates. Clean ^{1}H and ^{13}C NMR spectra were obtained for the cations **15e**, **15g**, **15i**, **15j**, and **15k** with all signals assigned. To illustrate, the ^{13}C NMR spectrum of cation **15e** is shown in Figure 6. The ^{13}C NMR chemical shifts of carbon atoms C_1, C_2, and C_3 are given in Table 2. As previously observed for *para*-methoxy-substituted benzylic carbocations,[8g,27] two sets of signals were visible in the ^{13}C NMR spectra of cations **15j** and **15k**, whereas cation **15g** showed broad signals for the aromatic *ortho*- (C_B) and *meta*- (C_C) carbon atoms. The alkyl-substituted cations (X = Me) **15e** and **15i** exhibited only a single set of signals. The peak broadening or peak separation for the oxygen-substituted cations **15g**, **15j**, and **15k** suggests two diastereomeric structures resulting from the hindered rotation of the methoxy substitutent of the PMP group. The partial double bond character of the bond between the *para*-carbon atom C_D and the oxygen atom leads to a mixture of *E* and *Z* isomers.

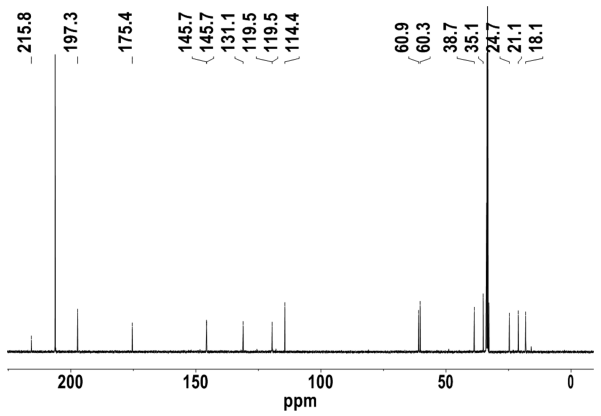


Figure 6. ^{13}C NMR spectrum of cation **15e** (acetone-d_6 as the external standard).

Table 2. Substitution Pattern and ^{13}C NMR Shift Data for Cations 15e, 15g, 15i, 15j, and 15k[a]

cation	X	R^2	C_1 (ppm)	C_2 (ppm)	C_3 (ppm)
15e	Me	*i*-Pr	197.3	114.4	215.8
15g	OMe	*i*-Pr	178.7	114.7	196.0
15i	Me	Et	197.3	114.4	215.1
15j	$OBnCl_2$	Et	179.9	116.1	198.2
15k	$OBnCl_2$	*i*-Pr	180.4	116.3	198.4

[a] FSO_3H–SO_2ClF, external standard acetone-d_6, and 193 K.

The described effect is well-precedented for PMP-substituted alkyl cations.[27] The rotational barrier around the C–O bond has been shown to be a benchmark for the stabilization of the respective cation by its adjacent substituents. It increases if nonbonding electron pairs of the oxygen atom are required for cation stabilization because of an inefficient stabilization by neighboring substituents.[28] For the present case, it follows[29] that the α-alkoxy-substituted cations **15g**, **15j**, and **15k** need to be additionally stabilized by the PMP group, while the alkyl-substituted cations **15e** and **15i** require less stabilization.

The significant deshielding of C_1 and C_3 relative to their alcohol precursors indicates a substantial mesomeric stabilization by the triple bond (allenyl cation as the resonance structure). When the chemical shifts are compared to those observed by Olah et al. for a tertiary, non-chiral propargylic carbocation of type **B** (Figure 1; R = Ph, R^1 = Me, and X and R^2 = H), we find good agreement with our results.[30] In this cation, carbon atoms C_1 and C_3 show a downfield shift to 199 and 237 ppm, respectively, which is in the same range as observed for cations **15e**, **15g**, **15i**, **15j**, and **15k**. Carbon atom C_2 is less deshielded (δ = 124 ppm) than C_1 and C_3, which also matches our experimental data (Table 2).

On the basis of the relatively strong downfield shift of carbon atoms C_3 in cations **15g**, **15j**, and **15k**, bridged onium ions are unlikely as cyclic intermediates in the S_N1-type substitution reaction.[31] While a significant downfield shift would be

dx.doi.org/10.1021/ja411772n | J. Am. Chem. Soc. 2014, 136, 2851–2857

expected for the methoxy carbon atom or the benzylic methylene group in a bridged onium ion, a minimal shift of 4 ppm in the ^{13}C NMR spectrum for these atoms excludes the existence of a positive charged oxygen atom. Additional synthetic work (see the Supporting Information) supported the existence of a propargylic cation with a flexible linkage to its neighboring stereogenic substituent.

Apart from the constitutional information, it was also possible to extract some information about the conformation of the propargylic carbocations. The ^{1}H NMR spectrum of cations **15e**, **15g**, and **15k** were well-resolved, and a strong NOE contact was observed between the methyl group at the cationic carbon and the hydrogen atom at the stereogenic center. This contact supports a preferred conformation **15″** (Figure 2), as depicted in Figure 7 for cation **15g**.

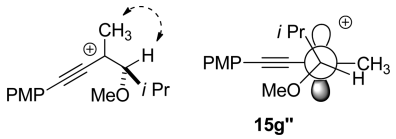
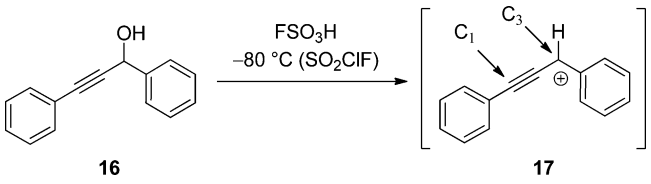


Figure 7. Preferred conformation of cation **15g** based on the indicated NOE contact.

In preliminary experiments toward the generation of secondary propargylic cations, we successfully prepared cation **17** from propargylic alcohol **16** (Scheme 8). The cation is the

Scheme 8



first secondary propargylic cation ever observed under superacidic conditions. However, it is evident by the chemical-shift data that the phenyl group at position C_3 significantly stabilizes the positive charge. The respective ^{13}C NMR chemical shifts for carbon atom C_1 (176.8 ppm) and carbon atom C_3 (178.1 ppm) are lower than those for the tertiary cations **15** discussed in the previous sections.

CONCLUSION

As a result of our study, the stereochemical outcome of S_N1-type substitution at various propargylic substrates with an α-stereogenic center ($-C^*HXR^2$) can now be understood. Intermediate cations are attacked in a conformation in which secondary or tertiary alkyl groups R^2 are positioned almost perpendicular (70−110°) to the plane defined by the three substituents at the cationic carbon atom. The hydrogen atom at the stereogenic center shows a dihedral angle Θ of 310−350° relative to the hydrogen atom at the secondary cation center. On the basis of DFT calculations, these conformations represent minima for secondary and tertiary cations. For tertiary propargylic cations, proof for the preferred conformation was obtained by NOE experiments. Attack occurs *anti* to the alkyl groups R^2 and leads to the respective *anti*-products with high selectivity (dr ≥ 90:10) for tertiary R^2 and with lower selectivity (dr ≅ 80:20) for secondary R^2 groups. It is surprising that the electronic influence of electron-donating groups (X = OMe and OCH_2Ar) is less pronounced. There is no indication for these groups to adopt a position perpendicular to the cation plane or to stabilize the cation via a non-bonding oxygen orbital. The former observation is striking given that alkoxy groups prefer a perpendicular position relative to the carbonyl group,[14a,32] in addition to reactions of strong nucleophiles to carbonyl compounds.[33]

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, characterization data for new compounds, X-ray crystallographic data, and details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project was supported by the Deutsche Forschungsgemeinschaft (Ba 1372/12-2) and by the Fonds der Chemischen Industrie (Kekulé scholarship to Dominik Nitsch and Liebig scholarship to Stefan M. Huber). The NMR studies were supported by the Loker Hydrocarbon Research Institute.

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