Chiral Benzylic Carbocations: Low-Temperature NMR Studies and Theoretical Calculations

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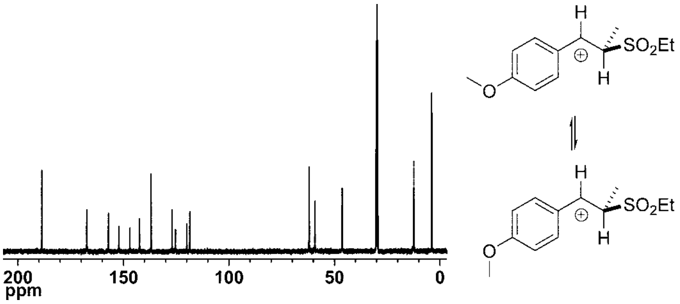

The α-chiral secondary and tertiary benzylic carbocations **19−30** were generated from the corresponding benzylic alcohols **1**, **2**, and **5−14** by treatment with FSO_3H or FSO_3H/SbF_5 in SO_2ClF as the solvent at −70 °C and characterized by one- and two-dimensional NMR spectroscopy. Coupling constants and NOESY measurements suggest a preferred conformation in which the α-hydrogen atom occupies the 1,3-allylic-strain position and the diastereotopic faces of the cations are differentiated by the alkyl substituent and a functional group (FG). The existence of this preferred conformation is further supported by calculations using a DFT method at the B3LYP/6-311+G** level. Quenching experiments with an arene nucleophile showed a preferential attack from the less shielded diastereotopic face delivering high diastereomeric ratios, supporting the hypothesis that these carbocations are involved as intermediates in previously studied S_N1 reactions. A strong shielding effect at the benzylic carbocationic center is observed for most of the secondary benzylic carbocations (derived from precursors **5−13**) investigated, indicating a strong mesomeric distribution of the positive charge to the carbon atom in the para-position of the anisyl substituent. For α-halogen-substituted carbocations (**5−7**, **12**), no neighboring halogen participation leading to halonium ion formation was observed.

Introduction

The first secondary benzylic cations were studied by ^1H NMR spectroscopy in solution as early as 1966.[1] The first ^{13}C NMR spectrum of such a cation was obtained in 1971.[2] Benzylic cations have been invoked as intermediates in many reactions, including Friedel−Crafts alkylation reactions,[3] [3 + 2]-cycloaddition reactions,[4] and rearrangements.[5] Possibly because of their high reactivity, chiral benzylic cations have not been extensively studied as intermediates in diastereoselective C−C bond forma-

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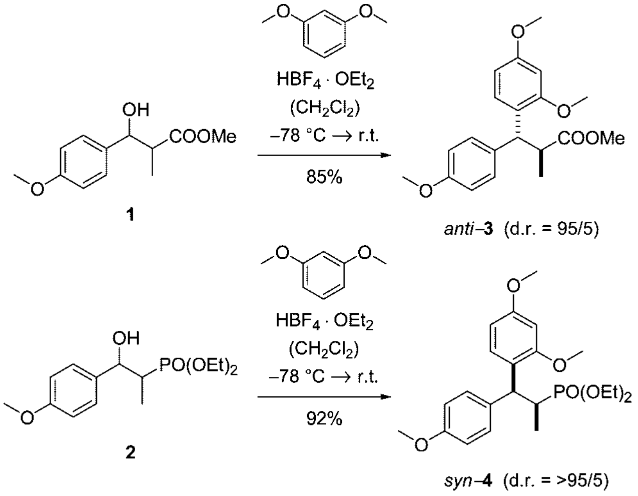
SCHEME 1. Diastereoselective Friedel−Crafts Alkylation Reactions via Chiral Benzylic Cations



tion reactions. The stereoselectivity in reactions of less reactive electrophiles (carbonyl compounds,[6] imines,[7] oxonium ions,[8] iminium ions[9]) has been elucidated in much more detail. Our knowledge about the major factors, which govern the diastereoselectivity in S_N1-type reactions[10] and in reactions which involve benzylic carbocations, lags behind the wealth of information which has been accumulated for, e.g., reactions of chiral aldehydes or ketones.[11]

Recently, we were able to show that chiral methoxybenzylic alcohols such as compounds **1** and **2**, which carry a functional group in the stereogenic α-position, react with various arenes in a highly selective fashion.[12,13] As an example, the reactions to the 1,1-diarylated products *anti*-**3** and *syn*-**4** are shown in Scheme 1. Chiral benzylic cations are likely intermediates in these reactions, and the question of how the selectivity of these reactions can be explained, led us to investigate the structure of the intermediates more closely under long-lived stable ion conditions.[14] In the present paper, we disclose full details on our NMR investigations of chiral benzylic cations, which bear a stereogenic center in the α-position. Evidence collected from DFT calculations and experiments suggests that the cations exist in a preferred conformation.

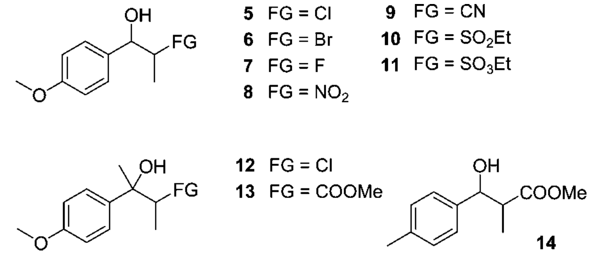
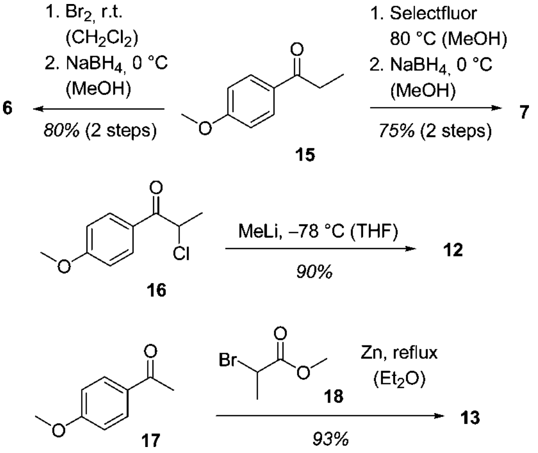


FIGURE 1. Set of secondary and tertiary benzylic alcohols **5**−**14** as cation precursors.

SCHEME 2. Preparation of the Starting Materials 6, 7, 12, and 13



Results and Discussion

Preparation of the Starting Materials. Our studies were conducted with the previously depicted benzylic alcohols **1** and **2** (Scheme 1) as cation precursors as well as with the alcohols **5**−**14** (Figure 1).

The synthesis of alcohols **1**, **2**, **5**, **8**−**11**, and **14** has already been reported.[12] 2-Bromoalkanol **6** and 2-fluoroalkanol **7** were prepared by a straightforward α-halogenation of the corresponding ketone **15** and subsequent $NaBH_4$ reduction (Scheme 2). For the fluorination, an extended reaction time (72 h) and a slight excess of Selectfluor (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis-tetrafluoroborate, 1.50 equiv) were required to reach full conversion. The product was not separable from the starting material by column chromatography. Methylmagnesium bromide addition to the known ketone **16**[15] at room temperature yielded only the undesired trisubstituted epoxide, whereas methyllithium addition at −78 °C prevented the epoxide formation and gave the corresponding tertiary 2-chloroalkanol **12** in good chemical yield. Precursor **13** was synthesized by a Reformatsky-type addition of methyl α-bromopropionate (**18**)[16] to ketone **17**.

Low-Temperature NMR Studies in Superacidic Media. Ionization experiments with different superacids (FSO_3H, FSO_3H/SbF_5, SbF_5) in different solvents (SO_2ClF, CD_2Cl_2) were undertaken to find the optimized conditions for the preparation

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SCHEME 3. Ionization of Precursors 1,2, and 5−11 and Generation of Cations 19−27 (Table 1) as a Mixture of Conformers (*E*/*Z*)

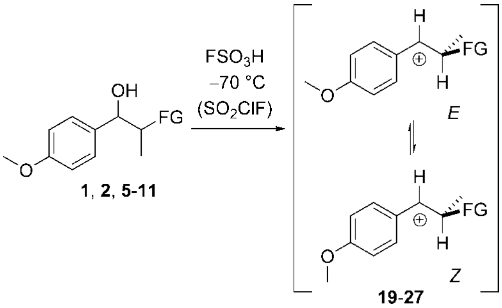
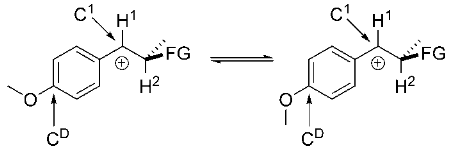


TABLE 1. Carbon Shifts for Major and Minor Conformers of Cations 19−27



cation	FG	C^1 (ppm) major[a]	C^1 (ppm) minor[a]	C^D (ppm) major[a]	C^D (ppm) minor[a]
19	Cl	180.6	180.5	187.0	187.0
20	Br	179.9	179.8	186.0	186.0
21	F	183.9	183.7	186.0	186.0
22	NO_2	170.0	170.9	188.2	188.3
23	CN	170.9	170.9	188.3	188.3
24	CO_2Me	172.1	172.1	188.1	188.1
25	$PO(OEt)_2$	172.2	172.2	188.1	188.2
26	SO_2Et	167.4	167.3	188.7	188.7
27	SO_3Et	168.1	168.1	188.5	188.6

[a] Major and minor conformer with respect to the orientation of the methoxy group.

of the carbocations. For all benzylic alcohols bearing a methoxy group in the para position (**1**, **2**, **5−13**), it turned out that FSO_3H in SO_2ClF was sufficiently strong to quantitatively generate the cations at −78 °C (Scheme 3). Generation of the carbocations in CD_2Cl_2 as the solvent was also successful, although FSO_3H is only poorly soluble at −78 °C and precipitated. Ionization with FSO_3H/SbF_5 (Magic Acid) or SbF_5 resulted only in decomposition probably due to protonation of the methoxy group and destabilization of the benzylic charge. If kept in SO_2ClF at −78 to −70 °C under superacidic conditions, the cations can be stored for several days without significant decomposition. Even short warming to higher temperatures (e.g., **5** to −30 °C) and cooling back to −70 °C did not result in significant degradation or side product formation indicating the relatively high stability of these intermediates.

Clean one- and two-dimensional NMR spectra including DEPT, COSY, NOESY, HMQC, and HMBC were obtained for the cations **19−27** allowing the full assignment of all signals (see the Supporting Information). The spectra showed two unequally populated structures for each carbocation resulting from the hindered rotation of the methoxy group of the anisyl substituent. The effect is due to the partial double bond character of the anisyl-carbon bond and a consequence of mesomeric stabilization (Table 1). The presence of *E*/*Z*-isomers in anisylalkyl cations is well precedented.[17] The *E*-conformer is normally the major diastereoisomer if the cation is secondary. The rotational barrier around the C−O bond has been used as a probe for the stabilization of the respective cation by various substituents. The rotational barrier increases if oxygen nonbonded electron pair assistance is required due to only weak stabilization by the direct cation substituents. On the other hand, if the cation stabilization is high, e.g., due to an adjacent cyclopropyl substituent, the rotational barrier decreases.[18] For tertiary carbocations (vide infra), bearing an additional methyl group in the benzylic position, both conformations are populated nearly equally. Interestingly, for all secondary carbocations **19−27** the carbon atom in the para position of the anisyl substituent (C^D) exhibited the most pronounced downfield shift, which was even more pronounced than the shift of the benzylic carbon atom C^1. This observation clearly shows that due to the electron-withdrawing properties of the functional group (FG) and the resulting destabilization of the positive charge in the benzylic position, the charge is strongly shifted to the methoxy-stabilized carbon atom in the para position of the anisyl ring.

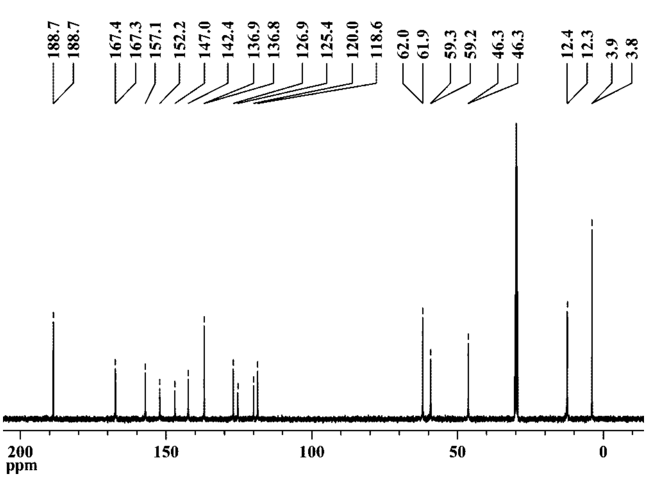


FIGURE 2. ^{13}C NMR spectrum of cation **26**.

Figure 2 shows a representative ^{13}C NMR spectrum of cation **26** recorded at −78 °C in SO_2ClF as the solvent. The two conformers are nicely identified in a ratio of 60/40. The aromatic methoxy-substituted carbon atom (C^D) is significantly deshielded appearing at 188.7 ppm for both conformers, while the benzylic carbon atom C^1 was found at 167.4 ppm in the major and at 167.3 ppm in the minor conformer. Acetone-d_6 was used as external standard ($\delta = 29.8$ ppm).

In the case of cations **19** (FG = Cl) and **20** (FG = Br), no evidence for the formation of bridged halonium ions by neighboring halogen participation was observed. The ^{13}C NMR chemical shift of carbon C^2 remains unchanged after ionization, i.e. by the transformations **5** → **19** and **6** → **20**. If halonium ion formation had occurred the carbon atom would have been significantly deshielded.[19] The result is in agreement with theoretical predictions and is in line with the fact that substitution reactions at alcohols **5** and **6** occurred with only modest diastereoselectivity.[12b,20]

Conformation Analysis. All ^1H NMR spectra showed a large ^3J coupling constant for H^1/H^2, which indicates an antiperiplanar

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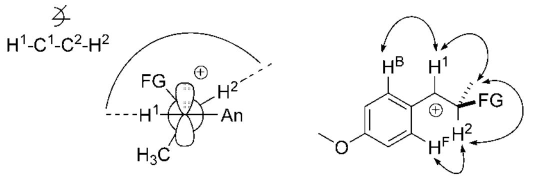


19-27

FIGURE 3. Newman projection defining the dihedral angle ($H^1-C^1-C^2-H^2$) and NOE contacts for cations **19**–**27** (An = anisyl).

TABLE 2. Observed Chemical Shifts and Calculated Dihedral Angles for Carbocations 19–**27**

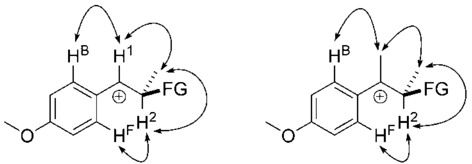
cation	FG	$^3J_{HH}$ (Hz) major[a]	$^3J_{HH}$ (Hz) minor[a]	calculated angle (°) monocation	calculated angle (°) dication
19	Cl	11.1	11.1	177	179
20	Br	11.8	11.8	175	176
22	NO_2	9.4	9.4	161	172
23	CN	10.3	10.4	175	169
24	CO_2Me	10.3	10.4	160	165
25	$PO(OEt)_2$	*b*	*b*	153	176
26	SO_2Et	10.8	10.8	156	165
27	SO_3Et	10.3	10.3	158	171

[a] Major and minor conformer with respect to the orientation of the methoxy group. [b] Coupling constant was not extractable due to $^3J_{HP}$-coupling.

relationship of these atoms. Taking into account that the empty p_z-orbital of the benzylic carbon atom C^1 must be parallel to the p_z-orbital of the anisyl ring to allow mesomeric stabilization, the hydrogen atom H^2 should be in the energetically favored 1,3-allylic strain position.[21] We have also fully optimized the structures at the DFT B3LYP/6−311+G** level using the Gaussian 03 program (see the Experimental Section). ^{13}C NMR chemical shifts were computed also by using Gaussian 03 program employing the GIAO method at the B3LYP/6-311+G**// B3LYP/6-311+G** level (vide infra). Indeed, geometry optimization calculations using the DFT method at the B3LYP/6-311+G** level showed a dihedral angle ($H^1-C^1-C^2-H^2$) of 153−177° for carbocations **19**–**27** (monocations).

On the left side of Figure 3 is depicted the conformation of cations **19**–**27** in the Newman projection, and the angle ($H^1-C^1-C^2-H^2$) is defined relative to the functional group FG and the methyl group. Indeed, according to the calculations, the angle as defined above varies in the cations between 156 and 179° (see Table 2) depending on the functional group FG and on its possible protonation (dication formation, vide infra).

The proposed conformation was further supported by 2D-NOESY spectra, in which single NOE contacts for H^1 and H^2 with the two different ortho hydrogen atoms H^B and H^F were observed. Typical NOE contacts are depicted on the right side of Figure 3 for the secondary cations **19**–**27** (Table 2). Most importantly, the contact between proton H^2 and the aromatic proton H^F supports the fact that the former proton resides in a 1,3-allylic strain position. The strong NOE of H^2 and H^F on one hand and of H^1 and H^B on the other are in accord with the previously mentioned antiperiplanar arrangement. It is evident from Figure 3 that the restricted rotation around the carbon−carbon bonds between cation center C^1 and anisyl substituent and between cation center C^1 and α-carbon atom C^2 lead to a differentiation of the diastereotopic faces at the very same cation center. The functional group FG resides at one diastereotopic face, the methyl group at the other, imposing a steric bias for the approach of a given nucleophile toward the electrophilic center.

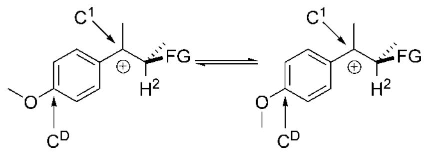


19-27 **28**, **29**

FIGURE 4. NOE contacts for cations **19**–**29**.

Tertiary Carbocations. Upon ionization of alcohols **12** and **13**, the tertiary benzylic cations **28** and **29** were obtained. The cations showed similar NMR-spectroscopic behavior as did their secondary analogues. Their stability was slightly higher due to the increased stabilization by the additional methyl substituent. The increased hyperconjugative stabilization is also responsible for a shift of the charge density from the methoxy-substituted aromatic carbon atom C^D to the cation center C^1. This fact is substantiated by the ^{13}C NMR chemical shifts of the respective carbon atoms, with C^1 now being more strongly deshielded as compared to C^D. The two conformers, which exist due to the restricted rotation around the C^D−OMe bond and which were unequally populated for the secondary cations **19**–**27**, are now equally populated. Relevant individual ^{13}C NMR chemical shift data are collected in Table 3.

TABLE 3. Carbon Shifts for Cations 28 and 29



cation	FG	C^{1a} (ppm)	C^{Da} (ppm)
28	Cl	203.5/203.5	184.3/184.3
29	CO_2Me	191.3/191.5	185.9/185.9

[a] Population of major and minor conformers is approximately 50/50.

The conformational preference concerning the dihedral angle ($CH_3{}^1-C^1-C^2-H^2$) appears—based on NOESY data—to be similar to the preference observed for the secondary cations (Figure 4). The antiperiplanar arrangement of the methyl group at C^1 and the proton H^2 at C^2 is deduced from strong NOE contacts of either proton to the ortho protons H^B and H^F in the anisyl substituent.

Variation of the Aromatic Substituent. Ionization of precursor **14** with FSO_3H in SO_2ClF resulted in incomplete cation formation due to the weaker stabilizing ability of the *p*-tolyl substituent. The red solution did not deliver conclusive spectra at −78 °C. It was, however, possible to achieve a clean ionization employing FSO_3H/SbF_5 in SO_2ClF as the acid system. Side reactions were suppressed due to the quantitative and rapid protonation by the stronger acid. The ^{13}C NMR spectrum of the resulting cation **30** (Scheme 4, Figure 5) revealed three deshielded carbon atoms with chemical shifts at 188.3, 190.2, and 192.2 ppm.[22] The individual signals were assigned to the carbon atoms COOMe, C^1 and C^D, respectively. As per our subsequent discussion, it is highly likely that the carbonyl oxygen atom of the ester group is protonated and that cation **30** indeed is a dication.

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(21) Review: Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841–1860.

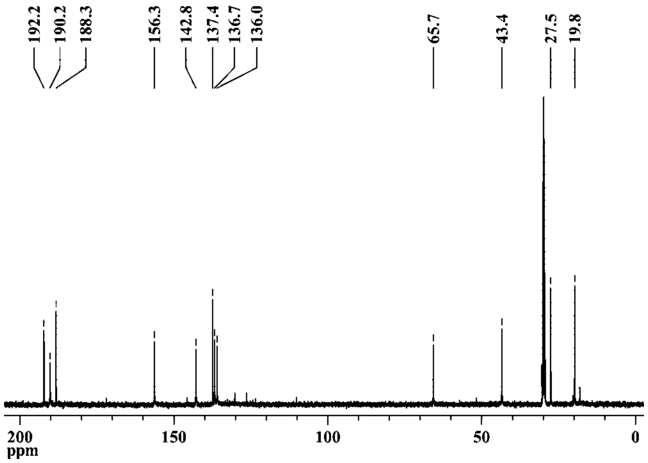
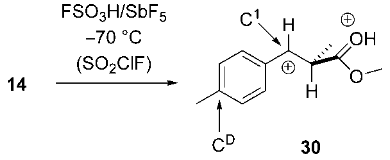


FIGURE 5. ^{13}C NMR spectrum of cation **30**

SCHEME 4. Ionization and Protonation of Precursor 14 with Magic Acid.



Other data obtained for cation **30** are in accord with previously studied tolyl cations.[22] The cation center at C^1 (δ = 190.2 ppm) is more strongly deshielded as compared to the same atom in the respective anisyl-substituted cation **24** (δ = 172.1 ppm). The coupling constant between H^1 and H^2 (^3J = 9.9 Hz) and the NOESY contacts (see Supporting Information) were similar to **24** indicating that cation **30** also adopts the preferred conformation previously discussed. The deshielded ^{13}C NMR signal for the ester carbonyl carbon atom (δ = 188.3 ppm) makes the formation of a dication as depicted in Scheme 4 highly likely.

TABLE 4. Chemical Shift Comparison of Functional Groups

precursor	FG	acid	chemical shift[a] (ppm) sm	carbocation
1	CO_2Me	FSO_3H	176.1	188.6
13	CO_2Me	FSO_3H	177.1	188.2
14	CO_2Me	FSO_3H/SbF_5	176.1	188.3 (^{1}H: 12.49)
9	CN	FSO_3H	121.0	112.0
2	$^{31}PO(OEt)_2$	FSO_3H	34.5[b]	33.9[b]
7	^{19}F	FSO_3H	−180.3[c]	−175.8[c]

[a] Major diastereoisomer (sm = starting material)/major conformer (carbocation). [b] ^{31}P NMR shift calibrated with PPh_3 as external standard. [c] ^{19}F-NMR shift calibrated with $CFCl_3$ as external standard.

TABLE 5. Carbon Shifts for Major Conformers of Cations 19−27

cation	FG	calcd shifts C^1 (ppm)	included scaling (X = 0.86)	obsd shifts C^1 (ppm)
19	Cl	195.0	167.7	180.6
20	Br	188.2	161.8	179.9
21	F	207.7	178.6	183.9
22	NO_2	197.3	169.6	170.0
23	CN	199.6	171.6	170.9
24	CO_2Me	213.4	183.5	172.1
25	$PO(OEt)_2$	205.4	176.6	172.2
26	SO_2Et	189.7	163.1	167.4
27	SO_3Et	195.7	168.2	168.1
28	Cl	220.0	189.2	203.5
29	CO_2Me	229.7	197.5	191.3

Investigations of Superelectrophilic Activation/Protonation of Functional Groups/DFT-GIAO Chemical Shift Calculations. Superacids are known to be sufficiently strong to generate, in some cases, very reactive dicationic species.[23] These systems can undergo reactions which would not be likely for the corresponding monocationic intermediates. Therefore, we investigated a possible subsequent protonation of the functional groups (FG) by comparison of their chemical shifts with the starting alcohols (Table 4). Typically, the chemical shift of the indicative atom decreased upon cation formation. While there is precedence that protonation indeed leads to a shielding at the former nitrile carbon atom,[24] we did not find any ^{19}F NMR or ^{31}P NMR data related to a possible protonation of fluorides or phosphonates. The relatively minor shift changes in cations **25** and **21** relative to their starting materials **2** and **7** make subsequent protonation of the functional group unlikely in FSO_3H, which is a relatively weak superacid. The carbonyl carbon atom in esters **1**, **13**, and **14**, however, exhibited a significant increase in ^{13}C chemical shift upon acid treatment, hinting at the protonation of the ester group. Additional evidence was based on the ^{1}H NMR of the cation derived from precursor **14**, in which an acidic proton was visible at 12.49 ppm, which would be perfectly in line with a protonated methyl carboxylate.[25]

These findings warranted calculation of the chemical shift data using the GIAO method at the B3LYP/6-311+G**// B3LYP/6-311+G** level (see the Experimental Section). The computed data were compared with the experimentally observed values. The calculated and experimental ^{13}C NMR chemical shifts of carbocationic (C^1) carbon of **19**−**27** are listed in Table 5. Calculated chemical shifts are substantially deviated from the experimental values. For example, ^{13}C NMR chemical shifts of carbocationic (C^1) carbon of **22** is 197.3, about 27 ppm more deshielded from that of experimental value of 170.0 ppm. Previous DFT calculations on a series of cumyl cations, however, indicated that the reasonable prediction of ^{13}C chemical shifts can be achieved through scaling as reported by Siehl et al.[26] Our present study shows that after scaling by a factor of 0.86, a reasonable correlation between predicted and experimental chemical shifts for a majority of carbocations **21**−**23** and **25**−**27** could be obtained. On the other hand, the agreement between experimental and theoretical values for halo-substituted carbocations **19**−**21** as well as carboxy-substituted cation **24** is rather poor. In ions **19**−**21**, the cationic centers are rather deshielded, ruling out any adjacent halogen participation. With the cation **24**, it appears that the ester group is also protonated in the FSO_3H medium. In the case of tertiary carbocations, the agreement between the calculated and experimental ^{13}C NMR

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(22) For tolyl-substituted carbocations, see: (a) Kelly, D. P.; Farquharson, G. J.; Giansiracusa, J. J.; Jensen, W. A.; Huegel, H. M.; Porter, A. P.; Rainbow, I. J.; Timewell, P. H. *J. Am. Chem. Soc.* **1981**, *103*, 3539–3543. (b) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666–2671. (c) Brown, H. C.; Periasamy, M.; Liu, K.-T. *J. Org. Chem.* **1981**, *46*, 1646–1650.

(23) (a) Olah, G. A.; Klumpp, D. A. *Acc. Chem. Res.* **2004**, *37*, 211–220. (b) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767–788. (c) Olah, G. A.; Klumpp, D. A. *Superelectrophiles and Their Chemistry*; Wiley: Hoboken, 2008.

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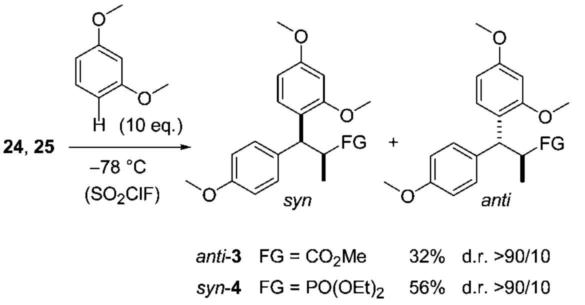
(25) (a) Bruck, D.; Rabinovitz, M. *J. Am. Chem. Soc.* **1976**, *98*, 1599–1600. (b) Walspurger, S.; Vasilev, A. V.; Sommer, J.; Pale, P.; Savechenkov, P. Y.; Rudenko, A. P. *Russ. J. Org. Chem.* **2005**, *41*, 1485–1492.

(26) Vrcek, V.; Kronja, O.; Siehl, H.-U. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1317–1321.

SCHEME 5. Results of the Quenching Experiments of Cations 24 and 25 with Resorcin Dimethyl Ether as a Representative Arene Nucleophile



chemical shifts of carbocationic (C^1) carbon of **29** is slightly better after scaling by the same factor of 0.86. On the other hand, halogen-substituted cation **28** does not correlate well at all even after scaling. It is important to mention that Siehl et al.[26] also showed that different scaling factors are necessary for different types of carbocations. Carbocations that are resonance stabilized (such as *p*-methoxy group substituted 2-phenyl-2-propyl cations) require different scaling factors than carbocations that are not resonance stabilized (such as alkyl-substituted carbocations).

Quenching Experiments. To further support the hypothesis that conformationally restricted carbocations **17−30** are reactive intermediates in our previously published Friedel−Crafts alkylation reactions, quenching experiments were undertaken with resorcinol dimethyl ether as a representative arene nucleophile (Scheme 5). Carbocations **24** and **25** were prepared at −78 °C according to the standard protocol in SO_2ClF as the solvent and were quenched with precooled rescorcin dimethyl ether (10 equiv). The typically strong color of the solution immediately vanished by addition of the nucleophile indicating a rapid reaction. Due to the high reactivity of the carbocations, several side products were formed resulting in only moderate yields for these reactions. Workup with saturated $NaHCO_3$ solution and separation by column chromatography gave the desired products *anti*-**3** and *syn*-**4** in almost identical diastereomeric ratios relative to the ratios obtained under our usual conditions (Scheme 1, $HBF_4 \cdot OEt_2$, −78 °C to rt).[12] The reaction of cation **24** delivered predominantly product *anti*-**3** with high diastereoselectivity, whereas cation **25** gave diastereoisomer *syn*-**4** almost exclusively.

Conclusions

In summary, the conformation of chiral *p*-methoxybenzylic cations bearing a stereogenic center of the general structure −C*HMeFG in the α-position were studied in the superacidic solution (FSO_3H or FSO_3H/SbF_5 in SO_2ClF). NOESY experiments showed that the hydrogen atom at the stereogenic center resides in the 1,3-allylic strain position with the methyl group shielding one diastereotopic face, the functional group FG the other. Such conformations are also supported by DFT theory. Due to the restricted rotation of the bond between the cationic carbon atom and the aryl group two rotamers exist, which could be separately observed. Indications for dication formation in superacids were found for COOMe as functional group with the ester carbonyl group likely being protonated. Quenching experiments strongly support the existence of benzylic carbocations as reactive intermediates in previously conducted Friedel−Crafts reactions. The diastereoselectivity results from a preferred conformation, in which the two faces of the cationic center are shielded differently by the methyl and FG substituents in the α-position.

Experimental Section

2-Bromo-1-(4′-methoxyphenyl)propane-1-carbenium Ion (20). Major conformer: ^1H NMR (400 MHz, −70 °C, SO_2ClF) δ = 1.32 (d, ^3J = 6.2 Hz, 3 H), 3.72 (s, 3 H), 4.84−4.95 (m, 1 H), 6.56−6.61 (m, 1 H), 6.74−3.81 (m, 1 H), 7.45 (d, ^3J = 11.8 Hz, 1 H), 7.66 (virt. t, $^3J \cong$ 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, −70 °C, SO_2ClF) δ = 21.7 (q), 39.6 (d), 60.6 (q), 117.8 (d), 125.5 (d), 129.7 (s), 141.9 (d), 157.8 (d), 179.9 (d), 186.0 (s). Minor conformer: ^1H NMR (400 MHz, −70 °C, SO_2ClF, e.s. acetone-d_6) δ = 1.32 (d, ^3J = 6.2 Hz, 3 H), 3.73 (s, 3 H), 4.84−4.95 (m, 1 H), 6.56−6.61 (m, 1 H), 6.74−3.81 (m, 1 H), 7.42 (d, ^3J = 9.4 Hz, 1 H), 7.45 (d, ^3J = 11.8 Hz, 1 H), 7.92 (dd, ^3J = 9.6 Hz, 1 H); ^{13}C NMR (100 MHz, −70 °C, SO_2ClF) δ = 21.7 (q), 39.6 (d), 60.7 (q), 118.4 (d), 124.8 (d), 129.5 (s), 146.3 (d), 152.9 (d), 179.8 (d), 186.0 (s).

2-Methoxycarbonyl-1-(4′-methoxyphenyl)propane-1-carbenium Ion (24). Major conformer: ^1H NMR (400 MHz, −70 °C, SO_2ClF) δ = 1.08 (d, ^3J = 6.6 Hz, 3 H), 3.77 (s, 3 H), 3.78 (s, 3 H), 4.05−4.16 (m, 1 H), 6.61 (d, ^3J = 9.7 Hz, 1 H), 6.77 (d, ^3J = 9.6 Hz, 1 H), 7.48 (d, ^3J = 10.3 Hz, 1 H), 7.56 (d, ^3J = 9.7 Hz, 1 H), 7.61 (d, ^3J = 9.6 Hz, 1 H); ^{13}C NMR (100 MHz, −70 °C, SO_2ClF) δ = 18.4 (q), 41.6 (d), 61.6 (q), 63.5 (q), 118.3 (d), 126.5 (d), 133.9 (s), 142.1 (d), 157.7 (d), 172.1 (d), 188.1 (s), 188.6 (s). Minor conformer: ^1H NMR (400 MHz, −70 °C, SO_2ClF, e.s. acetone-d_6) δ = 1.08 (d, ^3J = 6.6 Hz, 3 H), 3.76 (s, 3 H), 3.78 (s, 3 H), 4.05−4.16 (m, 1 H), 6.56 (d, ^3J = 9.5 Hz, 1 H), 6.83 (d, ^3J = 9.9 Hz, 1 H), 7.39 (d, ^3J = 9.5 Hz, 1 H), 7.48 (d, ^3J = 10.4 Hz, 1 H), 7.81 (d, ^3J = 9.9 Hz, 1 H); ^{13}C NMR (100 MHz, −70 °C, SO_2ClF, e.s. acetone-d_6) δ = 18.6 (q), 41.6 (d), 61.6 (q), 63.5 (q), 119.5 (d), 125.1 (d), 133.7 (s), 146.6 (d), 152.7 (d), 172.1 (d), 188.1 (s), 188.6 (s).

2-Ethylsulfonyl-1-(4′-methoxyphenyl)-propane-1-carbenium Ion (26). Major conformer: ^1H NMR (400 MHz, −70 °C, SO_2ClF) δ = 0.71 (t, ^3J = 6.9 Hz, 3 H), 1.09 (d, ^3J = 5.6 Hz, 3 H), 2.66 (q, ^3J = 6.9 Hz, 2 H), 3.75 (s, 3 H), 4.31−4.41 (m, 1 H), 6.58 (d, ^3J = 9.6 Hz, 1 H), 6.74 (d, ^3J = 9.6 Hz, 1 H), 7.11 (d, ^3J = 10.8 Hz, 1 H), 7.50 (d, ^3J = 9.6 Hz, 1 H), 7.55 (d, ^3J = 9.6 Hz, 1 H); ^{13}C NMR (100 MHz, −70 °C, SO_2ClF) δ = 3.9 (q), 12.3 (q), 46.3 (t), 59.2 (d), 61.9 (q), 118.6 (d), 126.9 (d), 136.9 (s), 142.4 (d), 157.1 (d), 167.4 (d), 188.7 (s). Minor conformer: ^1H NMR (400 MHz, −70 °C, SO_2ClF) δ = 0.71 (t, ^3J = 6.9 Hz, 3 H), 1.09 (d, ^3J = 5.6 Hz, 3 H), 2.66 (q, ^3J = 6.9 Hz, 2 H), 3.75 (s, 3 H), 4.31−4.41 (m, 1 H), 6.53 (d, ^3J = 9.5 Hz, 1 H), 6.81 (d, ^3J = 9.8 Hz, 1 H), 7.11 (d, ^3J = 10.8 Hz, 1 H), 7.32 (d, ^3J = 9.5 Hz, 1 H), 7.74 (d, ^3J = 9.8 Hz, 1 H); ^{13}C NMR (100 MHz, −70 °C, SO_2ClF) δ = 3.9 (q), 12.4 (q), 46.3 (t), 59.3 (d), 62.0 (q), 120.0 (d), 125.4 (d), 136.8 (s), 147.0 (d), 152.2 (d), 167.3 (d), 188.7 (s).

3-Methoxycarbonyl-2-(4′-methoxyphenyl)butane-2-carbenium Ion (29). Conformer A: ^1H NMR (400 MHz, −70 °C, SO_2ClF) δ = 1.06 (d, ^3J = 6.5 Hz, 3 H), 2.11 (s, 3 H), 3.71 (s, 3 H), 3.81 (s, 3 H), 4.41−4.51 (m, 1 H), 6.53−6.60 (m, 1 H), 6.72−6.79 (m, 1 H), 7.62 (d, ^3J = 9.7 Hz, 1 H), 8.03 (d, ^3J = 10.0 Hz, 1 H); ^{13}C NMR (100 MHz, −70 °C, SO_2ClF): δ = 16.0 (q), 20.7 (q), 46.3 (d), 60.7 (q), 63.9 (q), 117.3 (d), 124.4 (d), 133.1 (s), 142.2 (d), 149.2 (d), 185.9 (s), 188.2 (s), 191.3 (d). Conformer B: ^1H NMR (400 MHz, −70 °C, SO_2ClF) δ =1.06 (d, ^3J = 6.6 Hz, 3 H), 2.11 (s, 3 H), 3.71 (s, 3 H), 3.81 (s, 3 H), 4.41−4.51 (m, 1 H), 6.53−6.60 (m, 1 H), 6.72−6.79 (m, 1 H), 7.78 (d, ^3J = 9.9 Hz, 1 H), 7.86 (d, ^3J = 10.0 Hz, 1 H); ^{13}C NMR (100 MHz, −70 °C, SO_2ClF) δ = 16.1 (q), 20.9 (q), 46.3 (d), 60.7 (q), 63.9 (q), 117.7 (d), 124.7 (d), 133.1 (s), 144.7 (d), 146.6 (d), 185.9 (s), 188.2 (s), 191.5 (d).

1-(4′-Methylphenyl)-2-methoxycarbonylpropane-1-carbenium Ion (30): ^1H NMR (400 MHz, −70 °C, SO_2ClF) δ = 1.11 (d, ^3J = 7.0

Hz, 1 H), 2.15 (s, 3 H), 3.86 (s, 3 H), 4.20−4.31 (m, 1 H), 7.11 (d, ^3J = 8.7 Hz, 2 H), 7.56 (d, ^3J = 8.7 Hz, 1 H), 7.65 (d, ^3J = 8.7 Hz, 1 H), 8.23 (d, ^3J = 9.9 Hz, 1 H), 12.49 (s, 1 H); ^{13}C NMR (100 MHz, −70 °C, SO_2ClF) δ = 19.8 (q), 27.5 (q), 43.4 (d), 65.7 (q), 136.0 (d), 136.7 (d), 137.4 (s), 142.9 (d), 156.3 (d), 188.3 (s), 190.2 (d), 192.1 (s).

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Supporting Information Available: Experimental procedures for the preparation of new compounds and for the quenching experiments; ^{1}H and ^{13}C NMR spectra and data of all carbenium ions. Cartesian coordinates and total energies (hartrees) of the optimized geometries of **19−29** calculated at the B3LYP/6-311+G**//B3LYP/6-311+G** level. This material is available free of charge via the Internet at http://pubs.acs.org.

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