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Stable Ion and Electrophilic Chemistry of the Sterically Crowded Stilbene 1,1′-Bi(benzocyclobutenylidene) and Its Derivatives

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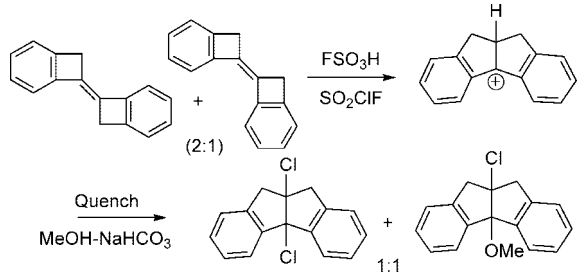

Generation and NMR studies of novel carbocations and carboxonium ions are reported from sterically hindered stilbene 1,1′-bi(benzocyclobutenylidene) **1**, its dimethoxy derivative **5**, and from their skeletally rearranged derivatives, namely, the spirocyclic ketone **6**, diastereomeric alcohols **7** and isomeric diols **8**. Quenching experiments on the carbocations under various conditions resulted in the formation/isolation of several novel covalent adducts. Acid-catalyzed isomerization of the diols **8** produced a remarkable dimeric molecule, whose structure was confirmed by X-ray analysis. Reactions of hindered stilbenes **1** and **5** with $Br_2/CDCl_3$ were examined via NMR experiments. The experimentally observed carbocations were also studied computationally by GIAO-DFT and by NICS.

Introduction

In 2002, Lenoir and associates reported on the synthesis of sterically hindered stilbene 1,1′-bi(benzocyclobutenylidene) **1** (Figure 1) by McMurry coupling of benzocyclobuten-1-one, resulting in a 1:1 mixture of *cis* and *trans* isomers, along with the isomeric diols **2**, which were obtained as minor products. The pure *trans* isomer of **1** was isolated on small scale by semipreparative HPLC or by crystallization techniques.[2] The X-ray structure of *trans*-**1** showed that the molecule is planar.[1] Photophysical and photochemical properties of the *trans* isomer along with a series of other cyclic stilbenes were investivated.[1,2]

An earlier reported approach to the synthesis of **1** by Dürr et al.[3] involved pyrolyis of the tosylhydrazone of benzocyclobuten-1(2*H*)-one, leading to a low yield of the *E*- and *Z*-isomers, along with several other products, whose identities were later established by Frimer et al.[4] Using a Wittig reaction as the key step of a multistep synthesis, Barton and Sheppard[5] synthesized stilbene **1** by reacting the triphenylphosphine salt of 1-bromo-1,2-dihydrobenzocyclobutene with benzocyclobuten-1(2*H*)-one.

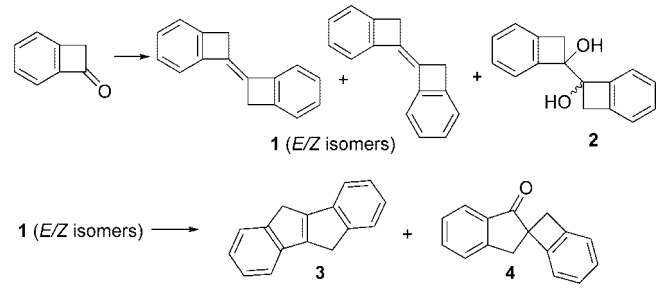

FIGURE 1. Synthesis of **1** (via McMurry coupling) along with isomeric diols **2** as byproduct, and formation of indene **3** and the spirocyclic ketone **4** in earlier studies reported in ref 5.

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(1) Oelgemöller, M.; Brem, B.; Frank, R.; Schneider, S.; Lenoir, D.; Hertkorn, N.; Origane, Y.; Lemmen, P.; Lex, J.; Inoue, Y. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1760–1771.
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(3) Dürr, H; Nickels, H.; Pacala, L. A.; Jones, M. *J. Org. Chem.* **1980**, *45*, 973–980.
(4) Frimer, A. A.; Weiss, J.; Rosental, Z. *J. Org. Chem.* **1994**, *59*, 2516–2533.
(5) Barton, J. W.; Shepherd, M. K. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1561–1565.

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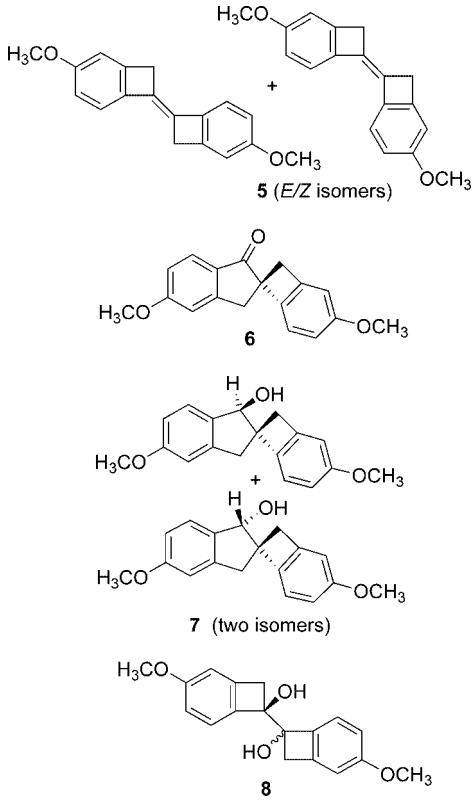


FIGURE 2. Compounds used in stable ion studies and in quenching and isomerization experiments.

Reaction of **1** with NBS resulted in bromination at the methylene groups in the four-membered rings, whereas reaction with Br_2 gave an isomeric mixture of dibromides by addition at the hindered double bond.[5] A rapid rearrangement was observed when **1** was reacted with Ac_2O containing sulfuric acid to give indene **3**, and reaction with selenium(IV) oxide led to the formation of the spirocyclic ketone **4** (Figure 1).[5]

Whereas carbocation formation and rearrangements were proposed to account for the formation of **3** and **4** (Figure 1),[5] no stable ion studies have hitherto been undertaken on this stilbene skeleton or its related skeletal isomers to explore the electrophilic chemistry of these theoretically interesting molecules. In relation to earlier stable ion and electrophilic addition studies on hindered alkenes from this laboratory,[6,7] we report here on the generation and chemistry of the carbocations/carboxonium ions via parent **1**, its dimethoxy derivative **5** (Figure 2), the spirocyclic ketone **6**, the diastereomeric alcohols **7**, and the isomeric diols **8**.

Results and Discussion

Bromination of 1,1′-Bi(benzocyclobutenylidene) 1 and 1,1′-Bi(methoxybenzocyclobutenylidene) 5: Compounds **1** and **5** (both prepared by McMurry coupling of the corresponding benzocyclobutene-1-one; see ref 1 and Experimental Section) were obtained as mixtures of *trans* and *cis* isomers in 2:1 ratio (by NMR analysis) (Chart S1 and Figures S2 and S3). On the basis of DFT (Table S1), the *trans* isomers of **1** and **5** are more stable relative to their corresponding *cis* isomers by 0.4 and 0.3 kcal/mol, respectively.

Since reaction of **1** with Br_2/CCl_4 was only briefly described in ref 5, at the onset, we performed a direct NMR study of the

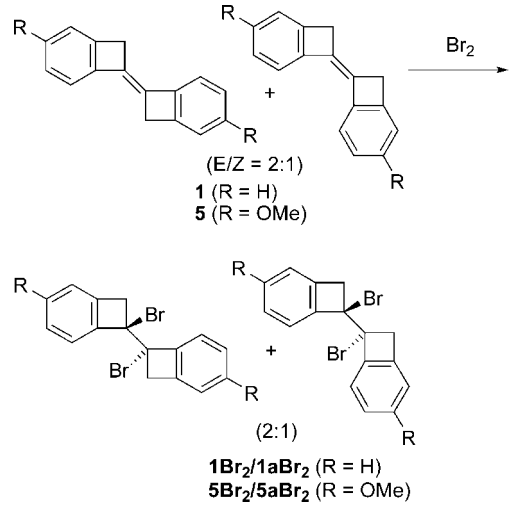


FIGURE 3. Bromination of **1** and **5**.

reactions of **1** and **5** with bromine in $CDCl_3$. Rapid bromination occurred at rt to form the corresponding dibromo compounds **1Br$_2$/1aBr$_2$** and **5Br$_2$/5aBr$_2$** as diastereomeric pairs (Figure 3). In a control experiment, addition of excess bromine into the NMR tube containing **1Br$_2$/1aBr$_2$** did not result in further bromination. In an independent experiment, **1** was allowed to react with a large excess of bromine under the same conditions. NMR monitoring again indicated rapid formation of **1Br$_2$/1aBr$_2$**, and no further bromination was observed. Similar results were obtained in the bromination of **5**, leading to **5Br$_2$/5aBr$_2$**. ^{13}C NMR data for the dibromo derivatives (not reported in ref 5) are gathered in Chart S1. In the room temperature ^{13}C NMR spectrum, sterically congested CH_2 (four-membered ring) is noticeably broadened in **1Br$_2$/1aBr$_2$** (Figure S4) due to hindered rotation around the central C−C bond, becoming undetectable in **5Br$_2$/5aBr$_2$** (Figure S5). Reaction of **5** with an excess amount of bromine gave a complex mixture of several products, with NMR indication for bromination occurring also at a phenyl ring.

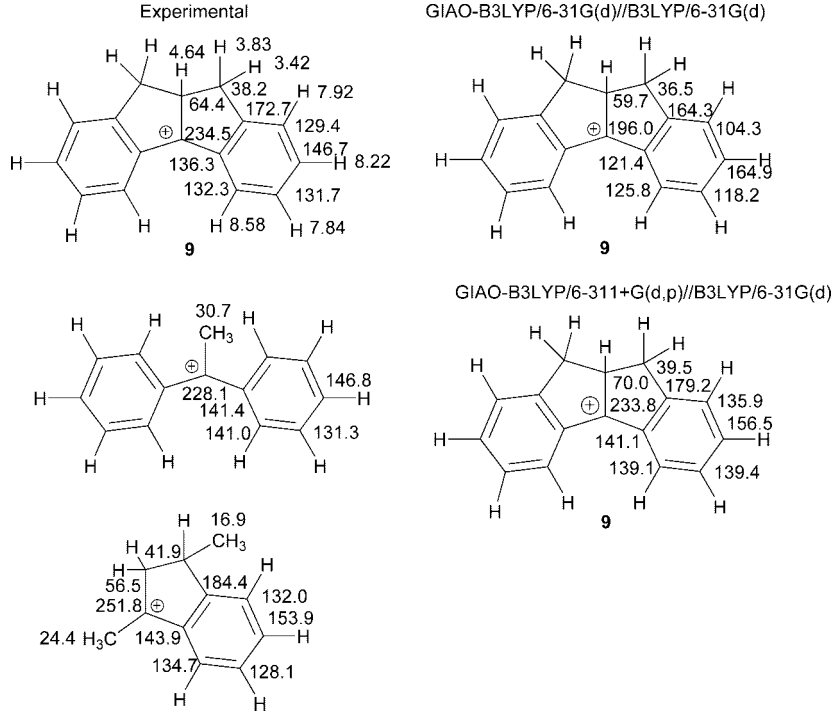
Protonation of 1,1′-Bi(benzocyclobutenylidene) 1 and Quenching Experiments: Low temperature reaction of **1** (2:1 *E/Z* mixture) with FSO_3H/SO_2ClF at dry ice/acetone temperature gave a reddish-yellow solution, whose NMR spectral data were consistent with the formation of the rearranged carbocation **9** as the sole species (Figure 4).

Specific assignments were made with the help of 2D NMR techniques (Chart 1). The doubly benzylic carbocation center is observed at 234.5 ppm (Figure S6). The reported values are at 228.1 ppm for the diphenylethyl cation[8] and 251.8 ppm for the indenyl cation.[9] Positive charge is extensively delocalized into the phenyl rings. The GIAO-derived ^{13}C data for **9** were computed employing 6-31G(d) and 6-311+G(d,p) basis sets (Chart 1), with the latter producing a closer fit with experiment.

Quenching of the superacid solution **9** with ice/$NaHCO_3$ followed by quick extraction (CH_2Cl_2) led to the formation of 9,10-dihydroindeno[1,2-*a*]indene **10**[10] in 33% yield (Figure 4a). A different quenching outcome resulted in experiments in which

(6) Laali, K. K.; Gano, J. E.; Gundlach, C. W.; Lenoir, D. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2169–2173.
(7) Laali, K. K.; Okazaki, T.; Takeuchi, K.; Ogawa, K.; Bennet, A. J. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1105–1111.
(8) (a) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *6*, 2729–2736. (b) Ancian, B.; Membrey, F.; Doucet, J. P. *J. Org. Chem.* **1978**, *43*, 1509–1518.
(9) Olah, G. A.; Asensio, G.; Mayr, H. *J. Org. Chem.* **1978**, *43*, 1518–1520.

CHART 1. Experimental and GIAO-Derived NMR Data for 9 and Comparison with Related Models



the extraction step was performed several hours after quenching (or in the next day). In these cases, the dichloro adduct **11** and the chloro alcohol adduct **12** were isolated (in 1:1 ratio) (Figures S7 and S8). A similar carbocation quenching procedure, using MeOH/bicarbonate, resulted in the formation of the dichloro adduct **11**, along with the chloromethoxy derivatives **13** (1:1 ratio) (Figure S9). These results indicate that, if not quickly isolated, the initially formed **10** undergoes further reaction, namely, Cl addition (via SO_2ClF),[11] followed by nucleophilic attack by water or MeOH to give the isolated products.

Scheme 1 illustrates various carbocation rearrangements that could ensue starting from **14** (R = H). DFT concurs with experiment (Table S1 and Figure S1a), showing that formation of the doubly benzylic carbocation **9** is strongly favored, with

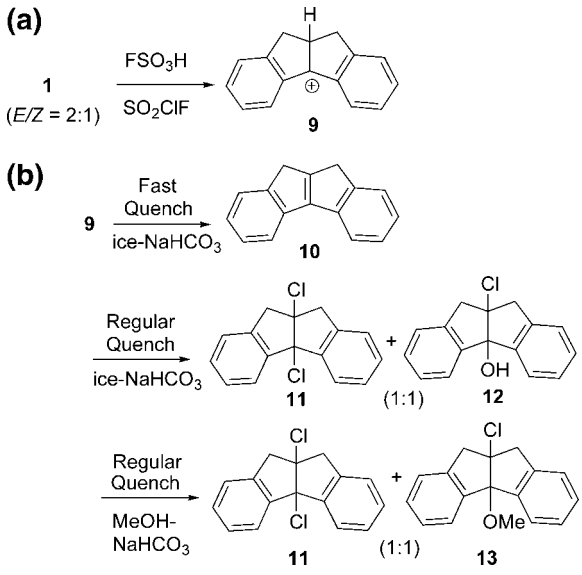
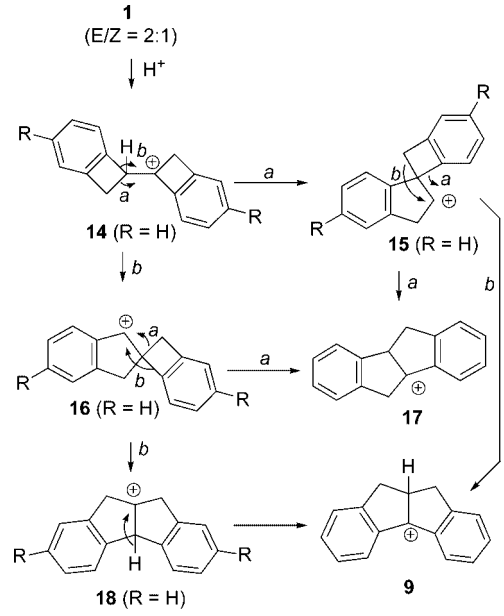


FIGURE 4. (a) Low temperature protonation of **1**. (b) Quenching experiments on carbocation **9**.

SCHEME 1. Possible Carbocation Rearrangement Pathways



the singly benzylic carbocation **17** lying 13.8 kcal/mol higher. The other carbocations constitute shallow minima en route to the observed **9**. As Figure S1a illustrates, with **14** as the initially fomed carbocation, ΔG continuously decreases in the sequences **14** > **16** > **18** > **9** and **14** > **16** > **17**.

Protonation of 1,1′-Bi(methoxybenzocyclobutenylidene) 5: Low temperature reaction of **5** (2:1 *E/Z* mixture) with FSO_3H/SO_2ClF at dry ice/acetone temperature gave a reddish-yellow solution, whose NMR spectral data were consistent with the formation of carbocations **19** and **20** (or **20a**) in approximately 1:1 ratio (Figure 5). The obtained spectra are similar to those of carbocations from alcohols **7** in FSO_3H/SO_2ClF (Figure 10, described later). Experimental and GIAO NMR data are sum-

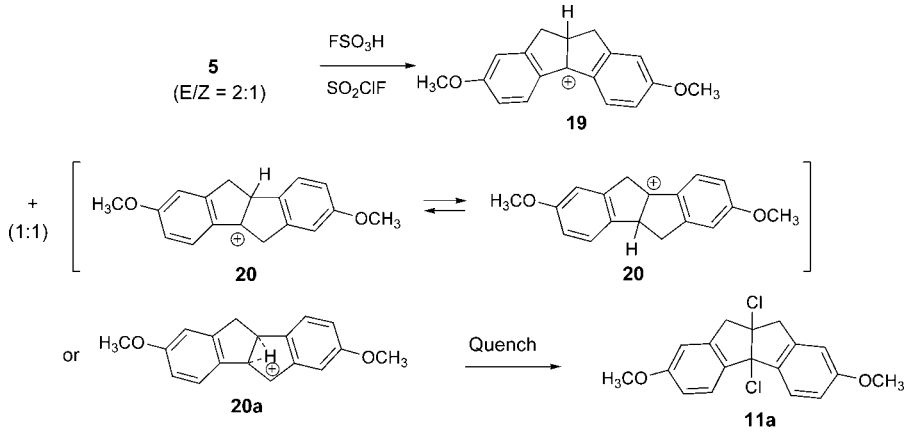
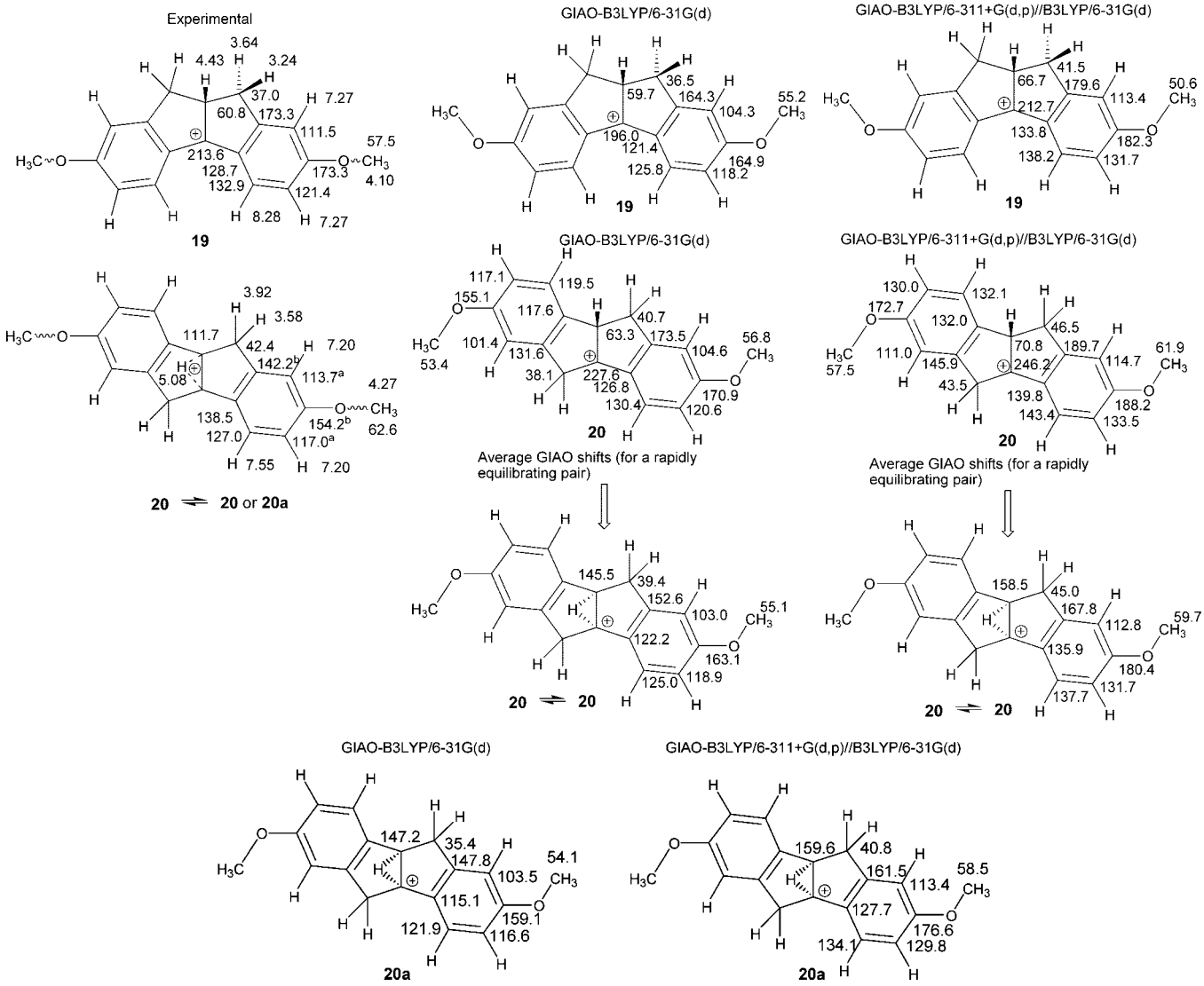


FIGURE 5. Low temperature protonation of **5** and quenching.

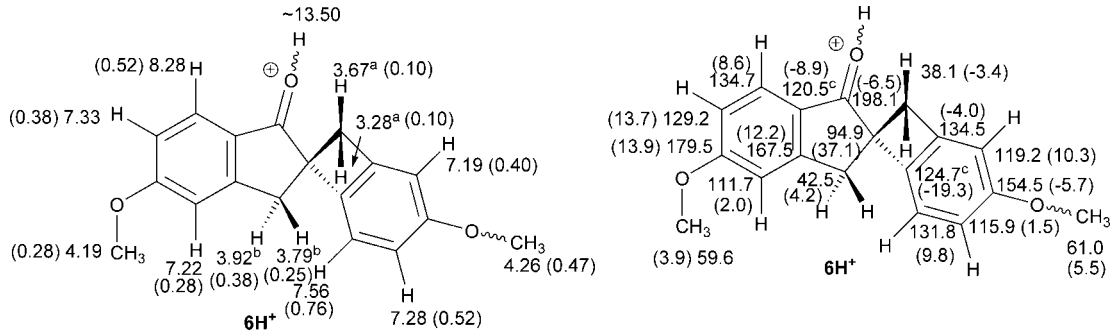
CHART 2. Experimental and GIAO NMR Data for Carbocations 19, 20, and 20a (a and b denote interchangeable assignments)



marized in Chart 2. The carbocation center in **19** is observed at 213.6 ppm, shielded by ca. 21 ppm relative to **9** due to methoxy back-bonding. Whereas the computed GIAO NMR data (see further) for a rapidly equilibrating pair **20** ⇌ **20** and a bridged structure (**20a**) were rather similar and did not allow a clear distinction, the bridged structure **20a** was characterized by DFT and by MP2 as a transition state (Table S1a; see also further discussion). On this basis, formation of a rapidly equilibrating pair appears more logical.

The equilibrating pair corresponds to carbocations **20** and **20a** in Table S1 (R = OMe), which on the basis of DFT are expected to be much less favored relative to **19**. Carbocations **19**, **20**,

CHART 3. ^{1}H and ^{13}C NMR Data for the Carboxonium Ion 6H$^+$ (a, b, and c refer to interchangeable assignments within each set; $\Delta\delta^{13}$C and $\Delta\delta^1$H relative to the corresponding parent compounds in parentheses)



and **20a** were computed by GIAO employing 6-31G(d) and 6-311+G(d,p) basis sets. For **19**, GIAO at higher basis set gave closer correspondence with the experiment. For the open structure **20**, the carbocation chemical shift was calculated at 227.6 and 246.2 ppm, depending on the basis set, with average chemical shift values of 145.5 and 158.5 ppm for a rapidly equilibrating pair. Finally, a symmetrically bridged cation **20a** was calculated as a transition state (lying 21.1 kcal/mol above **20** by B3LYP/6-31G(d)) (see energy plot included with Table S1a), and the computed chemical shift was 159.6 ppm by GIAO-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d).

Quenching of the superacid solution resulted in the isolation of the corresponding dichloro adduct **11a** (Figure S11). In the following sections, it is shown that the same carbocations are formed by ionization of the isomeric alcohols **7** (see Figure 2).

Relative Aromaticity in the Tetracyclic Carbocations by NICS: Skeletally rearranged tetracyclic carbocations **9**, **19**, **17**, and **20** were computed by NICS to gauge their relative aromaticity. The component of magnetic shift tensor in the z direction, which is perpendicular to the phenyl ring, NICS(1)$_{zz}$, was computed at 1 Å above and below the center of the phenyl rings. The results are depicted in Chart S2.

Extensive π-participation in the doubly benzylic carbocation **9** decreases the aromaticity of the benzo rings, relative to benzene computed by the same basis set.[12] In the singly benzylic carbocation **17**, the conjugated ring is relatively less aromatic. Methoxy substitution (**19** and **20**) notably decreases the aromaticity of the conjugated ring by enhancing π-participation while moderately decreasing the relative aromaticity of the nonconjugated ring.

Stable Ion Study of Isomeric Diols 8: The diastereomeric diols **8** (2:1 ratio) were formed as byproduct in the synthesis of **5** via McMurry coupling (Figure S12). When **8** was reacted with FSO_3H/SO_2ClF at dry ice/acetone temperature, the spirocyclic carboxonium ion **6H**$^+$ was formed (a red solution) (Figure 6). The NMR spectra were similar to those of carbocations from ketone **6** (shown later). The *C*OH$^+$ signal was observed at 198.1 ppm, and CO*H*$^+$ was detectable as a broad signal at ~13.50 ppm (Chart 3). It is notable that the formally sp^3-hybridized spiro carbon in the carboxonium ion is deshielded by 37.1 ppm relative to **6**.

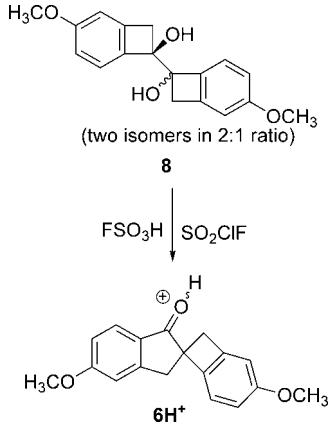


FIGURE 6. Low temperature protonation of diols **8**.

Acid-Catalyzed Isomerization of Diols 8: Reaction of diastereomeric diols **8** with trifluoroacetic acid TFAH in CH_2Cl_2 at 0 °C resulted in the formation of spirocyclic ketone **6** as major product and the dimeric product **21** as minor product (Figures 7 and S13). Whereas formation of a dimeric structure **21** was suggested via electrospray MS (as well as NMR), ultimate proof of the structure for this novel molecule came from X-ray analysis (Figure 7a with additional information in Supporting Information). Structure of **21** was also optimized by DFT for comparison (Figure 7b). The central dioxane unit adopts a chairlike conformation with nonequivalent C−O bonds and the bicyclo-[3.3.0]octadiene units are not C_s symmetrical.

Formation of dimer **21** may be traced back to carbocation **19** as key intermediate and its covalent products thereof, likely via a condensation reaction between the corresponding indene and the corresponding TFAH quenching adduct of carbocation **19**. Alternatively, compound **21** could be formed via dimerization of **8aH**$^+$ (Figure 8).

Protonation of Spirocyclic Ketone 6 and Quenching: Synthesis and isolation of **6** via acid-catalyzed isomerization of diols **8** provided an independent route to generation of **6H**$^+$. Thus low temperature reaction of **6** with FSO_3H/SO_2ClF (Figures 9 and S15) gave a yellow-orange solution, whose NMR spectra were the same as those obtained for **6H**$^+$ formed via protonation of diols **8** (Chart 3).

Quenching of the superacid solution of **6H**$^+$ with ice/$NaHCO_3$ afforded mainly the ring-opened ketone **22**, together with intact **6** as a minor product (Figures 9 and S16). Structure of the ring-opened ketone was determined by 2D NMR and by comparison with spectral data for the unsubstituted ketone in the literature.[13] A plausible pathway to the formation of **22** by exothermic

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(11) (a) Laali, K. K.; Okazaki, T.; Mitchell, R. H.; Ayub, K.; Zhang, R.; Robinson, S. G. *J. Org. Chem.* **2008**, *73*, 457–466. (b) Grenier-Loustalot, M. F.; Iratcabal, P.; Meitras, F.; Petrissans, J. *Synthesis* **1976**, 33–35. (c) Olah, G. A.; Ohannesian, L.; Arvanaghi, M.; Prakash, G. K. S. *J. Org. Chem.* **1984**, *49*, 2032–2034.

(12) Mills, N. S.; Llagostera, K. B. *J. Org. Chem.* **2007**, *72*, 9163–9169.

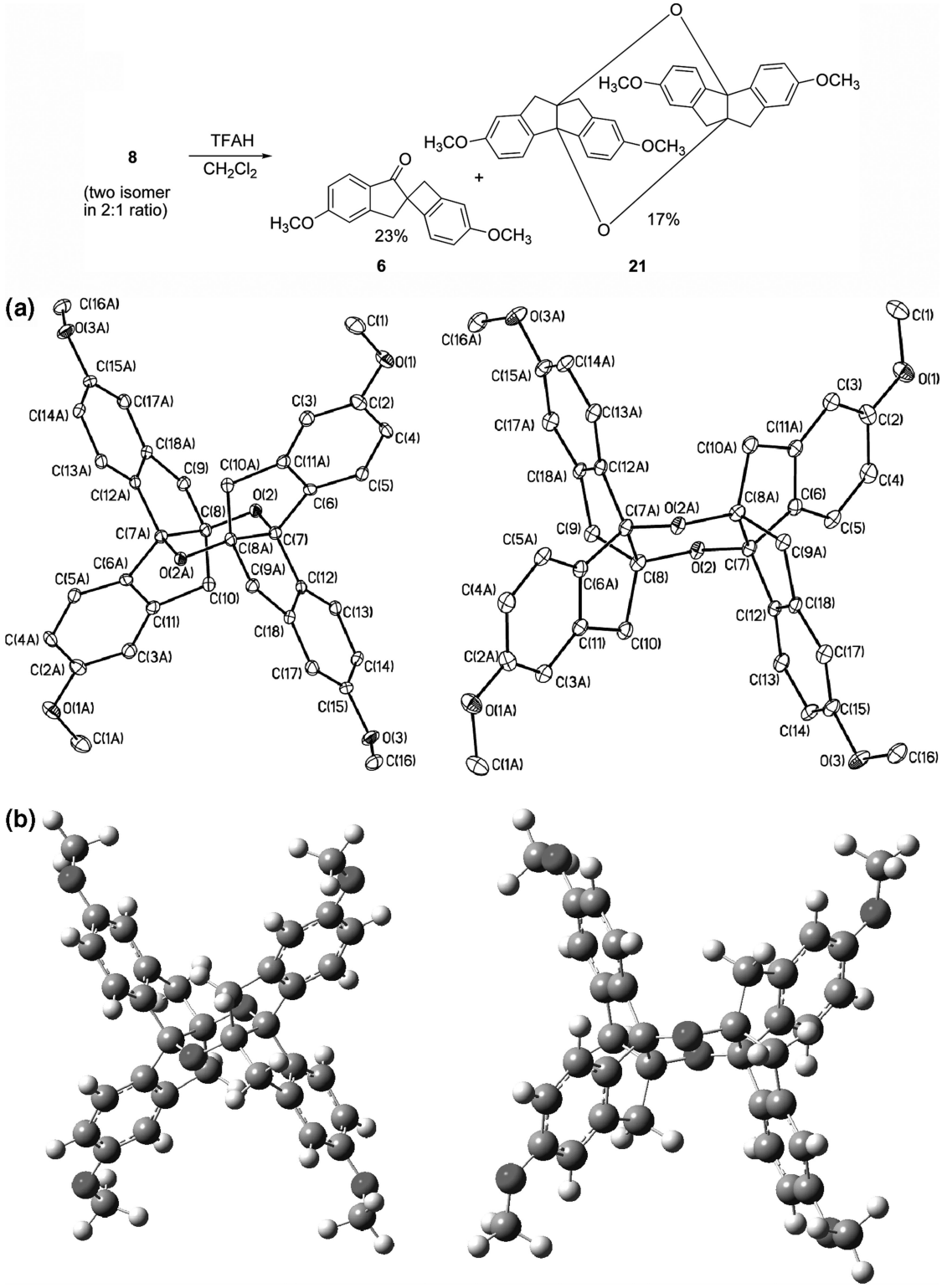

FIGURE 7. Top: Acid-catalyzed isomerization of diols **8**. (a) Molecular structure of the dimer **21** by X-ray analysis (ORTEP drawings; two different views). (b) DFT-optimized structure for **21**.

quenching is via a 1,3-migration of hydrogen in an electrocyclic process (although a radical process can not be ruled out).

Synthesis of Diastereomeric Alcohols 7 by Reduction of 6. The spirocyclic ketone **6** was reduced with LAH to produce a diastereomeric mixture of alcohols **7** in a 78:22 ratio by NMR (Figures 10 and S17).

Since attempted separation of diastereomers by silica chromatography led to decomposition, the mixture was directly reacted with FSO_3H/SO_2ClF at low temperature to give a yellow-orange solution. NMR spectra were consistent with the formation of carbocations **19** and **20** (in 1:1 ratio), that is, the

(13) Chatani, N.; Kamitani, A.; Oshita, M.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 12686–12687. (a) Sabitha, G.; Reddy, G. S. K. K.; Reddy, K. B.; Yadav, J. S. *Synthesis* **2004**, 263–266.

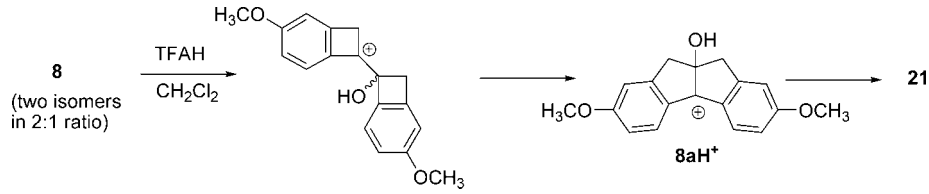

FIGURE 8. Plausible pathway to dimer **21**.

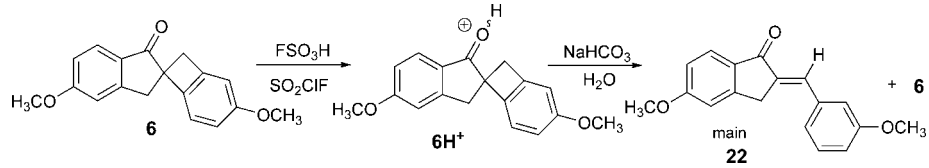

FIGURE 9. Protonation of **6** and quenching outcome.

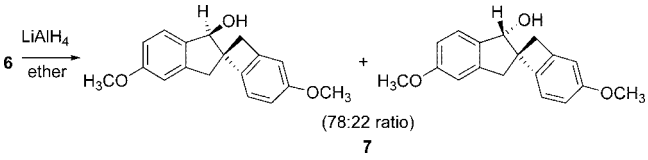

FIGURE 10. Reduction of spirocyclic ketone **6**.

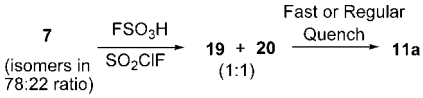

FIGURE 11. Protonation of **7** and carbocation quenching outcome.

same carbocation mixture formed by protonation of **5** (in Figure 5). The C*H* proton in **20** was observed at 5.08 ppm (Figure S18), and the carbocation center in **19** was detected at 213.6 ppm. Quenching of the superacid solution with ice/$NaHCO_3$ gave the dichloro adduct **11a** (Figure 11).

Cumulative Summary

Sterically crowded stilbenes **1** and **5** reacted with Br_2 to form the corresponding dibromo adducts by preferential addition to the hindered double bond. Under stable ion studies, in FSO_3H/SO_2ClF, the initially formed carbocation **14** escaped direct detection, rearranging rapidly to the doubly benzylic carbocation **9**. On the basis of DFT, the observed carbocation **9** is significantly more stable than **14** as well as other rearranged alternatives shown in Scheme 1. Novel covalent adducts **10**, **11**, **12**, and **13** were isolated in quenching experiments of **9**.

Low temperature protonation of **5** gave carbocation **19**, which is analogous to **9**, in addition to a second carbocation, whose experimental NMR data appeared compatible with a bridged structure **20a** or a rapidly equilibrating pair **20**. However, since **20a** was computed by DFT and by MP2 to be a transition state, and because the GIAO NMR data for **20** and **20a** were close at the studied basis sets, formation of a rapidly equilibrating pair was considered more likely. Quenching of the superacid solution led to the isolation of the covalent adduct **11a**.

Whereas skeletally rearranged tetracyclic carbocations **9**, **19**, **17**, and **20** are strongly aromatic as determined by $NICS(1)_{zz}$, the conjugated and/or substituted benzo rings in these structures are relatively less aromatic due to extensive π-conjugation and/or p-π back-bonding.

Isomeric diols **8**, which are formed as byproducts in the synthesis of **5** via McMurry coupling, undergo skeletal rearrangements upon superacid protonation, and this led to direct observation of carboxonium ion $\mathbf{6H}^+$. The same species was generated by independent protonation of the spirocyclic ketone **6**, which was isolated via quenching of $\mathbf{6H}^+$. Compound **6** was also formed as a main product in the solvolysis of diols **8** in TFAH. In this case, however, an intriguing dimer compound **21** was also obtained, whose structure was confirmed by X-ray analysis.

Low temperature protonation of the dimethoxy-substituted spirocyclic ketone **9** led to the formation of the carboxonium ion $\mathbf{9H}^+$. Upon quenching, the rearranged ketone **22** was isolated as the main product, together with the spirocyclic ketone **6** as minor product. The dimethoxy-substituted spirocyclic ketone **6** was reduced with LAH to a diastereomeric mixture of alcohols **7**, whose low temperature protonation provided another route to the formation of carbocations **19** and **20** which were formed via **5**.

Experimental Section

McMurry Reaction of 4-Methoxycyclobutenone: The ketone was prepared and supplied by P. Schiess (Basle);[14] $TiCl_4$ (5.07 g, 2.93 mL) was added dropwise to 150 mL of THF, while cooling with ice, 3.6 g of zinc dust was added gradually. To this mixture was added 3.61 g of the ketone precursor (25 mmol) dissolved in 10 mL of THF. The mixture was refluxed for 15 h. After cooling, a saturated solution of $NaHCO_3$ (100 mL) was added and the product mixture was extracted with methylene chloride (50 mL × 5). The organic phase was washed with water and dried over $MgSO_4$. After evaporation under vacuum, 3.1 g of crude product was obtained. Addition of *n*-hexane (100 mL) to the crude product mixture dissolved the *E/Z*-stilbenes **5**, together with some of the diols **8**. The separation was performed by flash chromatography on 100 g of silica using *n*-hexane/ethyl acetate (95:5) as eluent. A less polar fraction (0.2 g) was obtained consisting of an *E/Z* mixture of stilbenes **5**. The more polar fraction (0.5 g) consisted of the mixture of diols **8**.

(*E*)-**5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.83 (s, 2H), 3.83 (s, 6H), 3.63 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9 (2C), 145.6 (2C), 137.6 (2C), 124.1 (2C), 120.1 (2CH), 114.0 (2CH), 108.7 (2CH), 55.5 ($2CH_3$), 35.9 ($2CH_2$).

(*Z*)-**5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, J = 8.0 Hz, 2H), 6.81 (s, 2H), 6.78 (d, J = 8.0 Hz, 2H), 3.82 (s, 6H), 3.71 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0 (2C), 146.0 (2C), 137.5 (2C), 124.1 (2C), 120.0 (2CH), 114.1 (2CH), 108.7 (2CH), 55.5 ($2CH_3$), 36.7 ($2CH_2$).

8 *major*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J = 8.0 Hz, 2H), 6.68 (m, 4H), 3.77 (s, 6H), 3.32 (d, J = 14.0 Hz, 2H), 3.05

(14) Gokhale, A.; Schiess, P. *Helv. Chim. Acta* **1998**, *81*, 251–267.

(d, $J = 14.0$ Hz, 2H), 2.98 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0 (C), 143.2 (C), 139.0 (C), 122.9 (CH), 114.0 (CH), 108.3 (CH), 82.1 (C), 55.4 (CH_3), 42.2 (CH_2).

8 *minor*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, $J = 8.0$ Hz, 2H), 6.68 (m, 4H), 3.77 (s, 6H), 3.32 (d, $J = 14.0$ Hz, 2H), 3.08 (d, $J = 14.0$ Hz, 2H), 2.98 (br s, 2H). **8** *mixture*: ES-MS (negative ion mode, in CH_3CN without AgOTf) 297.2 $[M - H]^-$.

Computational Protocols: Structures were optimized by the density function theory (DFT) method at the B3LYP/6-31G(d) level using the Gaussian 03 package.[15,16] All computed geometries were verified by frequency calculations to have no imaginary frequencies except for **20a**, which had one imaginary frequency. Energies of the optimized structures for parent systems and their protonated cations are summarized in Table S1 in Supporting Information. In addition, **20** was calculated by B3LYP/6-311+G(d,p) and **20a** was computed by B3LYP/6-311+G(d,p) and by MP2/6-31G(d) (Table S1a).

NMR chemical shifts were calculated by the GIAO[17] method at the B3LYP/6-31G(d) and B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) levels. NMR chemical shifts were referenced to TMS (GIAO magnetic shielding tensor = 189.8 ppm at the B3LYP/6-31G(d) level and 184.1 ppm at the B3LYP/6-311+G(d,p) level in TMS; these values are related to the GIAO isotropic magnetic susceptibility for ^{13}C), calculated with molecular symmetry of T_d at the same level of theory. Nuclear independent chemical shifts (NICS)[12,18,19] were calculated at 1 Å above/below the ring center by the GIAO-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level. Their components in the z direction (assuming the z axis is perpendicular to the six-membered ring) were denoted as NICS$(1)_{zz}$. The ring centers were defined as the simple average of Cartesian coordinates for all the sp^2 carbons in the ring. The ring planes were calculated by least-squares methods using coordinates of all the sp^2 carbons in the ring.

Bromination of 1,1′-Bi(benzocyclobutenylidene) 1: Bromine was added into a solution of **1** (4 mg) in $CDCl_3$ (0.7 mL) until the color of bromine persisted. The resulting solution was analyzed by NMR, showing the formation of **1Br$_2$** and **1aBr$_2$** in a 2:1 ratio.

1Br$_2$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, $J = 8.0$ Hz, 2H), 7.24−7.16 (m, 4H), 7.09 (d, $J = 8.0$ Hz, 2H), 3.75 (br s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7 (2C), 139.8 (2C), 130.6 (2CH), 128.1 (2CH), 123.3 (2CH), 121.6 (2CH), 68.2 (2C), 47.8 ($2CH_2$).

1aBr$_2$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, $J = 8.0$ Hz, 2H), 7.24−7.16 (m, 4H), 7.07 (d, $J = 8.0$ Hz, 2H), 3.75 (br s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7 (2C), 139.4 (2C), 130.8 (2CH), 128.1 (2CH), 123.4 (2CH), 121.7 (2CH), 69.5 (2C), 47.8 ($2CH_2$).

Bromination of 1,1′-Bi(methoxybenzocyclobutenylidene) 5: Bromine was added into a solution of **5** (4 mg) in $CDCl_3$ (0.7 mL) until the color of bromine persisted. The resulting solution was analyzed by NMR, showing the formation of **5Br$_2$** and **5aBr$_2$** in a 2:1 ratio.

5Br$_2$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80−6.60 (m, 6H), 3.78 (s, 6H), 3.70 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (2C), 140.7 (2C), 135.4 (2C), 123.2 (2CH), 115.2 (2CH), 108.2 (2CH), 55.5 ($2CH_3$), 47.0 ($2CH_2$).

5aBr$_2$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80−6.60 (m, 6H), 3.78 (s, 6H), 3.70 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6 (2C), 135.4 (2C), 140.1 (2C), 123.2 (2CH), 115.2 (2CH), 108.2 (2CH), 55.5 ($2CH_3$), 47.0 ($2CH_2$).

Quenching of Carbocation 9 and Rapid Extraction (Method a): Compound **10**:[10] brown crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, $J = 7.5$ Hz, 2H), 7.52 (d, $J = 7.5$ Hz, 2H), 7.38 (t, $J = 7.5$ Hz, 2H), 7.23 (t, $J = 7.5$ Hz, 2H), 3.62 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7 (C), 148.0 (C), 147.9 (2C), 139.6, (2C), 126.4 (2CH), 124.6 (2CH), 124.4 (2CH), 119.5 (2CH), 35.7 ($2CH_2$).

Quenching of Carbocation 9 by Method b: Independent protonation of 1 (8.0 mg) with FSO_3H/SO_2ClF followed by quenching by method b gave a mixture of covalent adducts **11** and **12** in a 1:1 ratio which was purified by preparative TLC on SiO_2 with CH_2Cl_2/hexane (1:1) to afford **11** as a pale-yellow oil (0.5 mg, 5% yield) and **12** as a colorless crystalline solid (3.3 mg, 33% yield) ($R_f = 0.75, 0.05$).

Compound 11: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, $J = 7.0$ Hz, 2H), 7.34−7.26 (m, 4H), 7.20 (d, $J = 7.0$ Hz, 2H), 3.62 (d, $J = 16.5$ Hz, 2H), 3.32 (d, $J = 16.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0 (2C), 139.6 (2C), 129.0 (2CH), 127.8 (2CH), 125.0 (2CH), 124.6 (2CH), 96.5 (C), 84.3 (C), 45.8 (2C); ES-MS (+) 239.1 $[M - Cl]^+$.

Compound 12: Colorless crystals; mp 140.0−142.0 °C; IR (KBr) 3539, 3431, 2911, 1509, 1455, 1342, 1165, 1062, 783, 748, 729 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.56 (dd, $J = 8.0$ and 1.5 Hz, 2H), 7.28 (td, $J = 7.5$ and 1.5 Hz, 2H), 7.30 (br t, $J = 7.5$ Hz, 2H), 7.21 (d, $J = 7.0$ Hz, 2H), 3.59 (d, $J = 16.5$ Hz, 2H), 3.31 (d, $J = 16.5$ Hz, 2H), 2.91 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 142.0 (2C), 139.6 (2C), 129.0 (2CH), 127.9 (2CH), 124.8 (2CH), 124.6 (2CH), 91.8 (C), 84.3 (C), 45.8 ($2CH_2$); ES-MS (+) 618.0/620.9/622.9 $[M_2 + Ag]^+$, 363.1/365.1 $[M + Ag]^+$, 327.1/329.1 $[M + Ag - HCl]^+$, 221.2 $[M - Cl]^+$, 203.2 $[M - H_2O - Cl]$; MS/MS on m/z 618.0/620.9/622.9 → 363.1/365.1; MS/MS m/z 363.1/365.1 → 327.1/329.1, 221.2, 203.2.

Quenching by the method b (Supporting Information) using MeOH/sodium bicarbonate gave a mixture of **11** and **13** (1:1 ratio).

Compound 13: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, $J = 7.0$ and 1.5 Hz, 2H), 7.32−7.27 (m, 4H), 7.20 (d, $J = 7.0$ Hz, 2H), 3.56 (d, $J = 16.5$ Hz, 2H), 3.34 (d, $J = 16.5$ Hz, 2H), 3.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8 (2C), 140.0 (2C), 128.9 (2CH), 127.8 (2CH), 124.8 (2CH), 124.6 (2CH), 91.8 (C), 80.9 (C), 52.2 (CH_3), 48.5 ($2CH_2$).

Room Temperaure Acid-Catalyzed Isomerization of Diols 8: Trifluoroacetic acid was added into the solution of diols **8** (100 mg, 0.34 mmol) in CH_2Cl_2 (2.4 g) cooled in an ice−water bath. The initially formed pale-yellow suspension quickly changed into a reddish orange solution, which was quenched with ice−water. The resulting mixture was extracted with CH_2Cl_2, and the removal of the solvent gave a brown oil, which was purified by SiO_2 column chromatography, yielding the dimeric product **21** (8 mg, 17% yield) as colorless crystals using CH_2Cl_2 as solvent, and the spirocyclic ketone **6** (44 mg, 23% yield) as pale-yellow crystals by using CH_2Cl_2/ether (8:2) as solvent.

Compound 6: Mp 134.0−135.0 °C; IR (KBr) 1696, 1596, 1268, 1260, 1089, 1022, 847 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, $J = 8.0$ Hz, 1H), 6.95 (dd, $J = 8.0$ and 2.0 Hz, 1H), 6.94 (br s, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.79 (br s, 1H), 6.76 (dd, $J = 8.0$ and 2.0 Hz, 1H), 3.91 (s, 3H), 3.79 (s, 3H), 3.57 (d, $J = 14.0$ Hz, 1H), 3.54 (s, 2H), 3.17 (d, $J = 14.0$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.6 (C), 165.6 (C), 160.2 (C), 155.3 (C), 144.0 (C), 138.5 (C), 129.4 (C), 126.1 (CH), 122.0 (CH), 115.5 (CH), 114.4 (CH), 109.7 (CH), 108.9 (CH), 57.8 (C), 55.7 (CH_3), 55.5 (CH_3), 41.5 (CH_2), 38.3 (CH_2), ES-MS (+) 667.0/668.9 $[M_2 + Ag]^+$, 387.1/389.1 $[M + Ag]^+$, 280.3 $[M]^+$.

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Compound 21: Mp >290 °C; IR (KBr) 2930, 1607, 1494, 1263, 1108, 1082, 1028, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, $J = 8.5$ Hz, 4H), 6.73 (dd, $J = 8.5$, 2.0 Hz, 4H), 6.48 (d, $J = 2.0$ Hz, 4H), 3.70 (s, $4CH_3$), 3.29 (d, $J = 16.5$ Hz, 4H), 2.81 (d, $J = 16.5$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7 (4C), 142.3 (4C), 136.0 (4C), 125.0 (4CH), 113.6 (4CH), 109.6 (4CH), 87.2 (2C), 86.2 (2C), 55.2 ($4CH_3$), 44.2 ($4CH_2$); ES-MS (+) 667.4/669.2 $[M + Ag]^+$, 1226.8/1227.8/1228.8/1229.8 $[M_2 + Ag]^+$.

Quenching of $6H^+$: Starting with 12 mg of **6**, following low temperature protonation and normal quenching, the organic extract was separated by preparative TLC on SiO_2 with $CHCl_3$/hexane as eluent ($R_f = 0.20$) to give 12 mg of the ring-opened ketone **22** as pale-yellow oil, along with tiny amounts of intact **6**.

Compound 22: Mp 121.0−125.0 °C; IR (KBr) 1686, 1631, 1602, 1578, 1340, 1260, 1109 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.0$ Hz, 1H), 7.58 (t, $J = 2.0$ Hz, 1H), 7.37 (t, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 7.18 (br s, 1H), 6.99 (br s, 1H), 6.96 (dd, $J = 8.0$ and 2.5 Hz, 1H), 6.94 (dd, $J = 8.0$ and 2.5 Hz, 1H), 4.00 (br s, 2H), 3.92 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8 (C), 165.3 (C), 159.8 (C), 152.5 (C), 136.9 (C), 135.5 (C), 132.6 (CH), 131.4 (C), 129.8 (CH), 126.2 (CH), 123.1 (CH), 115.9 (CH), 115.3 (CH), 114.9 (CH), 109.7 (CH), 55.7 (CH_3), 55.3 (CH_3), 32.5 (CH_2); ES-MS (+) 667.0/669.0 $[M_2 + Ag]^+$, 387.1/389.1 $[M + Ag]^+$, 281.3 $[M + H]^+$; MS/MS on *m/z* 387.1/389.1 → 280.3.

Reduction of Spirocyclic Ketone 6 to Diastereomeric Alcohols 7: Ketone **6** (24 mg) was reduced with $LiAlH_4$ in dry ether at room temperature overnight under nitrogen atmosphere to give the corresponding isomeric alcohols **7** in near quantitative yields as a colorless oil (25 mg). The diastereomeric ratio was 78:22 by ^1H NMR. Attempted separation of the diastereomers by SiO_2 column chromatography led to decomposition. Specific NMR assignments of the diastereomers were made by 2D NMR and NOED spectra directly in the mixture.

Major Diastereomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, $J = 8.5$ Hz, 1H), 6.81 (m, 3H), 6.74 (br s, 1H), 6.71 (dd, $J = 8.5$ and 2.5 Hz, 1H), 5.11 (br s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.55 (d, $J = 14.5$ Hz, 1H), 3.32 (d, $J = 16.0$ Hz, 1H), 3.13 (d, $J = 16.0$ Hz, 1H), 2.28 (d, $J = 14.5$ Hz, 1H), 2.00 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2 (C), 160.0 (C), 144.0 (C), 142.9 (C), 140.9 (C), 135.9 (C), 125.1 (CH), 121.2 (CH), 113.3 (CH), 112.8 (CH), 110.2 (CH), 109.1 (CH), 79.6 (CH), 59.5 (C), 55.4 ($2CH_3$), 40.6 (CH_2), 36.4 (CH_2).

Minor Diastereomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, $J = 9.0$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.81 (m, 2H), 6.75 (m, 2H) 4.95 (br s, 1H), 3.82 (s, 1H), 3.79 (s, 1H), 3.42 (d, $J = 16.0$ Hz, 1H), 3.17 (d, $J = 14.0$ Hz, 1H), 3.08 (d, $J = 16.0$ Hz, 1H), 3.03 (d, $J = 14.0$ Hz, 1H), 1.79 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5 (C), 160.3 (C), 144.1 (C), 143.8 (C), 138.5 (C), 135.6 (C), 125.8 (CH), 123.0 (CH), 113.5 (CH), 112.9 (CH), 110.2 (CH), 109.4 (CH), 80.4 (CH), 59.7 (C), 55.4 ($2CH_3$), 41.4 (CH_2), 40.6 (CH_2).

Mixture: Colorless oil; IR (NaCl) 3420, 2921, 1607, 1471, 1261, 1106, 1028, 816 cm^{-1}; ES-MS (+) 671.0/673.0 $[M_2 + Ag]^+$, 389.1/391.1 $[M + Ag]^+$, 265.2 $[M - OH]^+$; MS/MS on *m/z* 389.1/391.1 → 264.3, 281.3, 280.3.

Protonation of Diastereomeric Alcohols 7 and Quenching. Following low temperature protonation of **7** (12 mg) and NMR study, the superacid solution was quenched according to method b to give the covalent adduct **11a** (2.4 mg, 18% yield) as colorless crystals.

Compound 11a: Mp 140.0−142.0 °C; IR (KBr) 2921, 1616, 1518, 1259, 1018, 817 cm^{-1}, ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, $J = 8.5$ Hz, 2H), 6.84 (dd, $J = 8.5$, 2.5 Hz, 2H), 6.72 (br s, 2H), 3.78 (s, 6H), 3.53 (d, $J = 16.5$ Hz, 2H), 3.25 (d, $J = 16.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5 (2C), 141.0 (2C), 134.5 (2C), 125.3 (2CH), 114.0 (2CH), 109.8 (2CH), 91.0 (C), 84.7 (C), 55.4 ($2CH_3$), 45.9 ($2CH_2$); ES-MS (+) 738.9/740.9/742.8 $[M_2 - Cl + Ag]^+$, 422.9/424.9/426.9 $[M - Cl + Ag]^+$, 387.0/389.0/391.1 $[M - Cl_2 + Ag]^+$; MS/MS on *m/z* 422.9/424.9/426.9 → 387.9/389.0 $[M - Cl_2 + Ag]^+$, 281.0/263.0 $[M - Cl_2]^+$.

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Supporting Information Available: Energies and Cartesian coordinates for the optimized structures, experimental NMR data for the neutrals, NICS valued for carbocations, general experimental methods, selected NMR spectra for carbocations and neutral compounds. Selected bond distances and angles for compound **21** from X-ray analysis, X-ray crystallographic file in CIF format for **21**, also available from the Cambridge Database under CCDC 675346. This material is available free of charge via the Internet at http://pubs.acs.org.

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