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Synthesis, Mechanism of Formation, and Dynamics of a Highly Fluorinated Methylenecyclobutene

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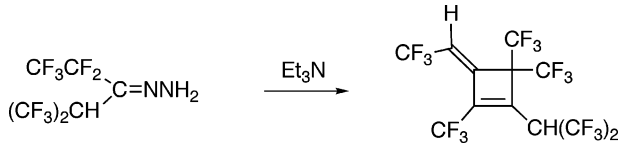
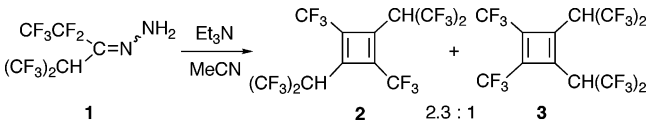


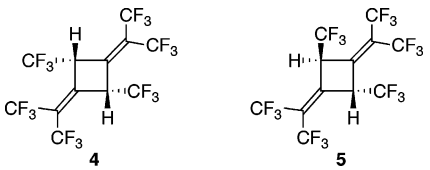
Treatment of the hydrazone of 2*H*-perfluoro-2-methyl-3-pentanone with triethylamine at elevated temperatures yields a methylenecyclobutene via degradation to an acetylene followed by dimerization. The dimerization occurs even at −78 °C, and details of the reaction pathway have been elucidated. Both the acidity and the conformational dynamics of the methylenecyclobutene are influenced by buttressing effects in this crowded molecule.

Introduction

As a minor observation at the end of an interesting paper on the synthesis of highly fluorinated heterocycles, Furin et al. reported that hydrazone **1** was transformed by triethylamine into a mixture of cyclobutadienes **2** and **3**.[1] The volatile liquid



mixture they obtained was characterized by ^{13}C NMR, ^{19}F NMR, MS, and HRMS. In light of the antiaromaticity of cyclobutadienes, we believed that if they were formed they would isomerize under the hot (80 °C) basic conditions to more stable tautomers. Formation of stereoisomeric dimethylenecyclobutanes **4** and **5** from **2**, for example, would be exothermic by 35.5 and 36.0 kcal/mol, respectively, according to AM1 calculations.[2]



(1) Furin, G. G.; Chi, K.-W.; Protsuk, N. I.; Lopyrev, V. A. *Zh. Org. Khim.* **2001**, *37*, 1693.

(2) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

Together with our long-standing interest in cyclobutadienes, this consideration stimulated us to repeat the reaction of hydrazone **1** with triethylamine.

Results and Discussion

Reaction Pathway. Under the conditions of Furin et al., the product we obtained had the expected molecular weight, but the ^{19}F NMR spectrum differed considerably from that in the literature. For **2** and **3**, signals were reported at δ −59.6 (6F) and −65.7 (12F) and δ −59.0 (6F) and −62.0 (12F), respectively, in $CDCl_3$. The ratio of **3** to **2** was reported to be 2.3:1 (by GC). We consistently observed four signals at δ −60.3, −63.5, −65.4, and −67.3 in the same solvent with relative areas 1:2:1:2, accompanied by small signals for impurities and/or isomers. No ^1H NMR spectrum had been reported, but we found proton resonances in $CDCl_3$ at δ 5.97 (q, J = 9 Hz, 1H) and 4.37 (m, 1H). The (H, F) COSY spectrum revealed that the low-field proton was coupled with the CF_3 group at −60.3 ppm and that the higher-field proton was coupled with two CF_3 groups at −63.5 ppm. These data point to the conclusion that there is a single compound, not two, and that the two pairs of stereoisomeric methylenecyclobutenes **6** and **7** and **8** and **9** are candidate structures. An (F, H) NOESY spectrum showed interaction of the high-field proton with the vinyl CF_3 on the ring (Figure 1), a finding expected for all four structures, but also with the geminal CF_3 groups on the ring, thereby ruling out structures **8** and **9**. The vinyl proton also interacted with the same geminal CF_3's but not with the vinyl CF_3 on the ring. Thus, the structure of the methylenecyclobutene is **6**.

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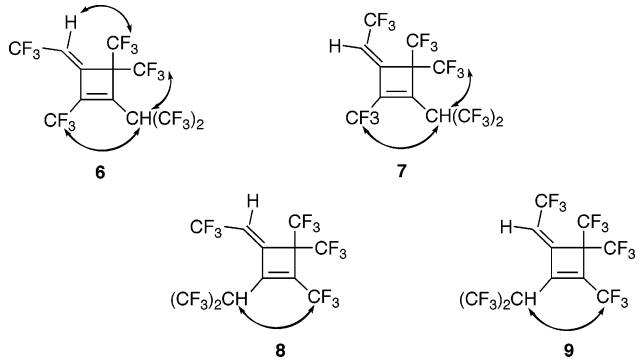
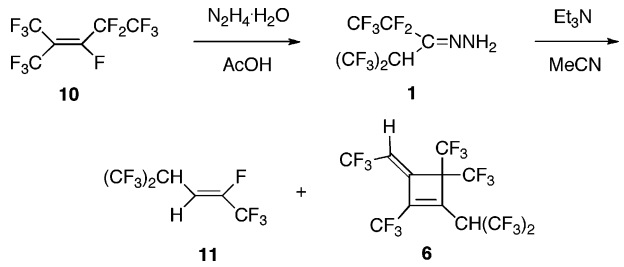
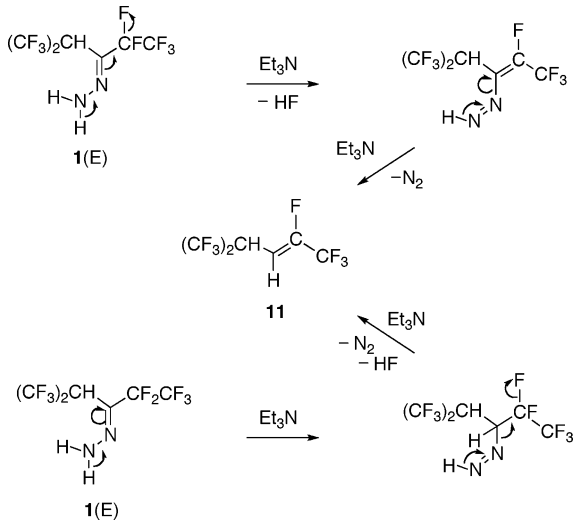


FIGURE 1. Arrows indicate sites for NOE interactions in the four candidate methylenecyclobutene structures.

SCHEME 1

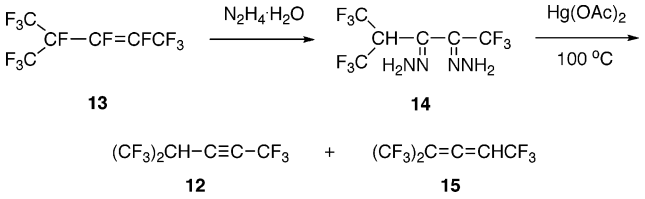


SCHEME 2



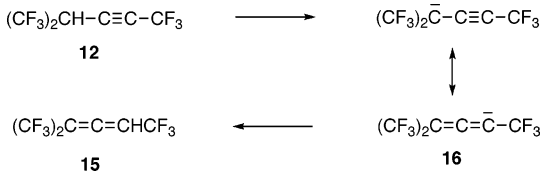
Prepared from alkene **10**, hydrazone **1** is a roughly 2:1 mixture of *E*- and *Z*-isomers.[1,3] When it is treated with triethylamine at room temperature, a small amount of **6** is obtained from the *E*-isomer, but the principal product is *Z*-vinyl fluoride **11** (Scheme 1).[4] Alkene **11** is formed readily from the *E*- but only slowly from the *Z*-hydrazone isomer. Alternative pathways from (*E*)-**1** to **11** are depicted in Scheme 2 (analogously for (*Z*)-**1** to **11)**. Formation of the *Z*-vinyl fluoride, exclusive of the *E*-vinyl fluoride, is understandable in light of the difference in F−F nonbonded repulsion in their respective transition states for fluoride elimination, whichever pathway is followed. At higher temperatures, formation of **11** goes to

SCHEME 3



completion and some of it undergoes elimination of a second equivalent of HF to give acetylene **12**, which had been proposed by the original workers as an intermediate in their reaction.[1] Though undetected in their work because it was lost in the workup, vinyl fluoride **11** is the major product (76% by NMR) under the reported reaction conditions (80 °C, 3 h), and that is true even when a large excess of triethylamine and longer reaction times are employed. Conditions sufficient to complete the dehydrofluorination of **11** lead to extensive decomposition.[5] Following the aqueous workup procedure in the literature, we were unable to obtain fluorocarbon **6** free of acetonitrile solvent, and the reported boiling range of 80−82 °C and 63% yield indicate that the product originally obtained was actually a solution of **6** in acetonitrile. Our boiling point for methylenecyclobutene **6** is 136 °C.

Starting with alkene **13**, we synthesized acetylene **12** via bishydrazone **14** and obtained it along with its more stable allene isomer **15** (Scheme 3).[6,7] The acetylene is stable in chloroform solution, but it spontaneously rearranges completely to the allene isomer in acetonitrile solution at room temperature. This transformation must occur via their common anion **16**, perhaps catalyzed by glass.



The acetylene and allene dimerize to methylenecyclobutene **6** under the reported reaction conditions and even at −78 °C. Because the dimerization proceeds in very high yield (by NMR) to give **6** together with much smaller amounts of other isomers, this is a better way to prepare the methylenecyclobutene. In principle, formation of **6** could occur via attack of anion **16** on a molecule of either the acetylene or the allene. We surmise that attack takes place on the allene not only because it dominates the tautomeric equilibrium but also because anionic attack on the allene yields a much better stabilized anion.

It is not obvious a priori which end of propargylic anion **16** carries out the attack, as the more hindered end is also the end that should sustain the greater negative charge. Thus, there are two pathways to methylenecyclobutene **6** to consider, as depicted in Scheme 4. Path A would be expected to lead to anion **17**, which upon workup would yield methylenecyclobutene **7**, with the wrong (*Z*) configuration at the exocyclic double bond. That is because the initial attack on the allene

(3) Ramanathan, S.; Lemal, D. M. *J. Org. Chem.* **2007**, *72*, 1566.

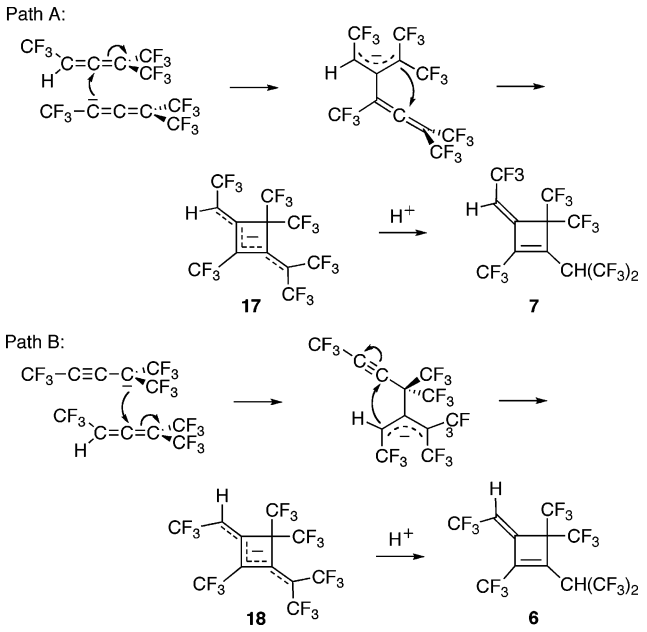
(4) The *Z* configuration was indicated by the $^3J_{HF}$ of 30 Hz and was confirmed by a NOESY experiment that revealed interaction between the isopropyl proton and the vinyl F and no interaction with the vinyl CF_3.

(5) Reaction of hydrazone **1** with other bases, such as DBN in acetonitrile and potassium *t*-butoxide in DMSO, gives even poorer results.

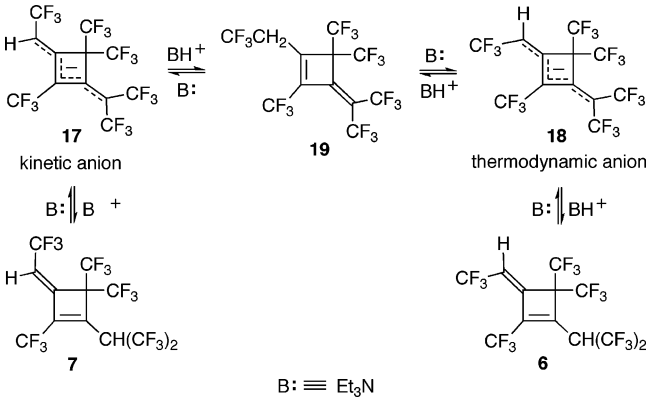
(6) Bargamov, G. G.; Mysov, E. I.; Bargamova, M. D. *Izv. Akad. Nauk, Ser. Khim.* **1994**, 2039.

(7) Bargamov, G. G.; Kagramanova, E. M.; Bargamova, M. D. *Russ. Chem. Bull.* **1998**, *47*, 656−658.

SCHEME 4



SCHEME 5



should be as shown, from the side of the hydrogen and not the bulky trifluoromethyl group that is geminal to it. Path B should yield methylenecyclobutene **6** after acidification, as addition to the triple bond should give the *E* anion **18**, as shown.

Path B was the clear choice until we discovered that triethylamine catalyzed the dimerization of acetylene **12** in acetone-d_6 even at −78 °C and that under these conditions the anion formed was **17**, not the expected **18**. When the reaction mixture was allowed to warm, as the temperature approached 0 °C, anion **18** appeared and ultimately replaced **17** completely. Thus, **17** is the product under conditions of kinetic control, but **18** is the thermodynamic anion, formed via methylenecyclobutene isomer **19** (Scheme 5) and/or directly via bond rotation in anion **17**.[8,9] When **17** is quenched with acid at low temperatures, mixtures of methylenecyclobutenes **6** and **7** are obtained, indicating equilibration of the two anions during the quenching process. Quenching of anion **18** leads exclusively to methylenecyclobutene **6**.

We conclude that dimerization of allene **15** proceeds via Path A, in which the less-hindered end of the propargylic anion **16** initiates the attack.

(8) At the B3LYP/6-31G* level of theory, $\Delta E_{17\rightarrow 18} = -2.79$ and $\Delta E_{6\rightarrow 7} = +0.47$ kcal/mol (0 K, uncorrected for zpe difference).

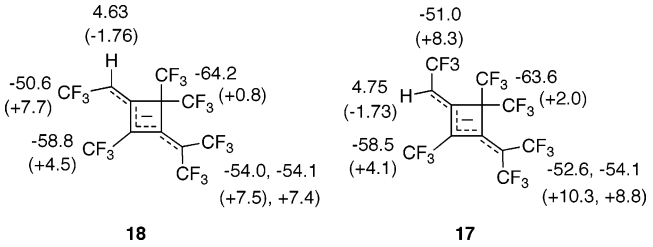
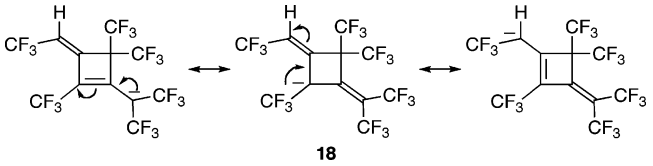


FIGURE 2. ^{19}F and ^{1}H NMR resonances of anions **18** and **17** in CD_3CN, together with their shifts (in parentheses) from the corresponding signals in methylenecyclobutenes **6** and **7**, respectively. The data for **17** were obtained at −44 °C, and the data for the others were obtained at room temperature. Triethylammonium was the counterion for **18** and **17**.

Acidity of Dienes 6 and 7. Reflecting the highly delocalized nature of its conjugate base **18**, diene **6** is deprotonated even by weak bases. If only a trace of weak base is present, **6**



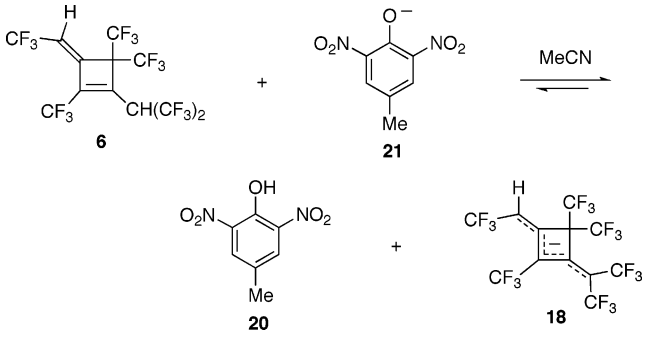
equilibrates with its stereoisomer **7** via the pathway in Scheme 5. In acetonitrile at room temperature, the ratio of **6** to **7** at equilibrium is ∼1.5:1.[8] The ^{19}F and ^{1}H NMR signals for their respective anions **18** and **17** in acetonitrile-d_3 are shown in Figure 2, along with the shifts from their positions in the conjugate acids. The chemical shift equivalent CF_3's of the hexafluoroisopropyl group in **6** and **7** have become inequivalent in the anion because of its rigidity. The vinyl proton in both isomers is shifted strongly upfield as expected, but all of the fluorine resonances are shifted downfield, dramatically so for the four CF_3 groups along the conjugated system. Thus, the paramagnetic contribution to the ^{19}F chemical shifts overwhelms the diamagnetic shielding, presumably because there are lower lying excited states in the anions than in the dienes.[10]

To obtain a measure of the acidity of diene **6**, we studied its acid−base equilibrium in acetonitrile with 2,6-dinitro-*p*-cresol (**20**). This phenol was chosen for three reasons: acidity comparable to that of **6**, a known pK_a in water (4.23),[11] and a conjugate base (**21**) that, like **18**, is highly delocalized. The fluorocarbon was found to be considerably more acidic than the phenol. Methylenecyclobutene **7** was also present at equilibrium in the mixture, but the concentration of its conjugate base **17** was too small to detect. Thus, **7** is much less acidic than **6**.

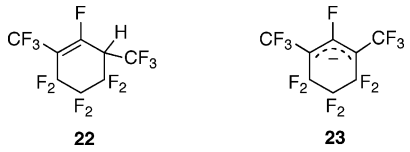
(9) All density functional calculations were carried out with: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(10) Lambert, J. B.; Mazzola, E. P. *Nuclear Magnetic Resonance Spectroscopy. An Introduction to Principles, Applications and Experimental Methods*; Pearson: Upper Saddle River, NJ, 2004; pp 80−81.

(11) Robinson, R. A. *J. Res. Natl. Bur. Stand., Sec. A* **1967**, *71*, 385.



The analogous equilibrium of cyclohexene **22** with the cresol had been examined at −45 °C in the same solvent, and the equilibrium constant was found to be ∼50.[12] Providing that this constant is not much smaller at room temperature, **22** is more acidic than diene **6**. The conjugate base **23** of cyclohexene **22** is only an allylic anion, and that of diene **6** is pentadienylic, with comparable fluorine substitution on the two conjugated systems. At first glance, the relative acidity is paradoxical but may be understood in light of conformational dynamics in the methylenecyclobutene that are discussed below.



Hindered Rotation in Diene 6. At room temperature, the four ^{19}F NMR signals for **6** are somewhat broad, suggesting the possibility of a dynamic process near its limit on the NMR time scale. When a dichloromethane solution of **6** was cooled in the NMR probe, by −46 °C, the four resonances had each decoalesced into two peaks of equal area. The ^{19}F chemical shift difference for each pair at −68.5 °C, roughly the slow exchange limit, is shown in Figure 3. The temperature dependence of the chemical shifts was determined to −105 °C, and extrapolation into the intermediate exchange region followed by line shape analysis revealed that $\Delta G^{\ddagger} = 11.8 \pm 0.1$ kcal/mol.

The process under observation is rotation about the bond to the hexafluoroisopropyl group, which exists in two conformations that happen to be virtually equal in energy. Their geometries calculated at the B3LYP/6-31G* level of theory appear in Figure 4. It is striking that the second largest chemical shift difference between rotamers corresponds to the CF_3 geminal to hydrogen, the group farthest from the rotating bond. Clearly, there is a significant buttressing effect in this molecule that makes all six CF_3 groups interdependent. One is reminded that CF_3 groups are quite bulky and larger in fact than isopropyl groups.[13]

This buttressing effect is also apparent in a comparison of the variable temperature behavior of **6** with its stereoisomer **7** having the *Z* configuration at the exocyclic double bond. Even at −50 °C, the four ^{19}F resonances of **7** are not significantly broadened, so the rotational barrier for its hexafluoroisopropyl group must be considerably lower than that in **6**. Repulsion exerted by the CF_3 on the exocyclic double bond in **6** against the CF_3 in the same plane acts as a more effective brake on the bond rotation than the repulsion exerted by the former CF_3 in **7** against the out-of-plane geminal CF_3 groups. However, equilibration of **6** and **7** at room temperature, as noted above, reveals that they differ little in energy, so the total steric repulsion in the two isomers must be very similar.

The substantial barrier to rotation in diene **6** arising from F−F nonbonded repulsion provides an explanation for the lower acidity of **6** as compared with cyclohexene **22**. The orientation of the rotating CF_3's in the transition state must not be too different from their location in the flattened anion, the calculated geometry of which is shown in Figure 5. Thus, steric destabilization of conjugate base **18** relative to diene **6** results in diminished acidity.

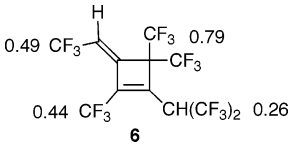


FIGURE 3. Differences in the ^{19}F chemical shift (ppm) between the signals for the two rotamers of methylenecyclobutene **6** in dichloromethane at −68.5 °C.

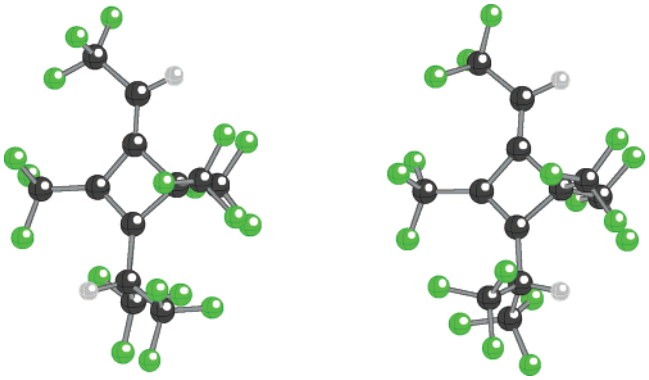


FIGURE 4. Geometries of the two rotamers of methylenecyclobutene **6** at the B3LYP/6-31G* level of theory.

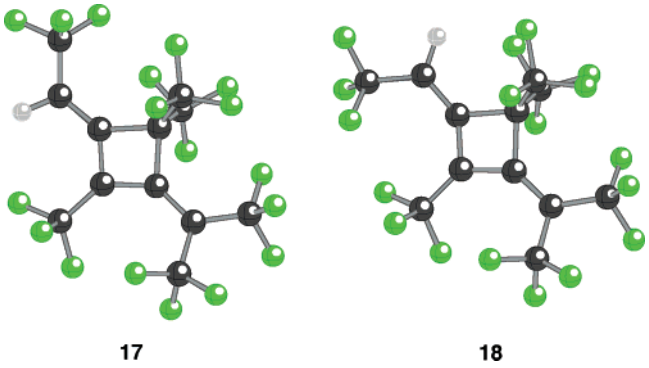


FIGURE 5. Geometry of anions **17** and **18** at the B3LYP/6-31G* level of theory.

Conclusion

Reaction of hydrazone **1** with triethylamine at elevated temperatures proceeds via vinyl fluoride **11**, acetylene **12**, and allene **15** to give methylenecyclobutene **6**, though **11** is the major

(12) Chen, X.; Lemal, D. M. *J. Org. Chem.* **2004**, *69*, 8205.

(13) The *A* values of the CF_3 and isopropyl groups are 2.4−2.5 and 2.21, respectively (Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; p 697). Their modified Taft steric values (E_s^o) are −2.40 and −1.71, respectively (Hansch, C.; Leo, A. *Substituent Constants for Correlation in Chemistry and Biology*; Wiley: New York, 1979).

product of the reaction. Starting with acetylene **12** made it possible to gain insight into the details of the dimerization process, as this reaction proceeds readily even at −78 °C. The initial product, anion **17**, equilibrates with the more stable anion **18**, from which **6** is obtained upon acidification.

Methylenecyclobutene **6** is a crowded molecule, the properties of which are strongly influenced by F−F nonbonded repulsions around its periphery. The effect of buttressing is evident in both a substantial barrier to rotation about a single bond and less-than-expected acidity. Stereoisomeric methylenecyclobutene **7**, though slightly higher in energy than **6**, has a considerably lower barrier to single bond rotation.

Experimental Section

(*E*)-1,3,3-Tris(trifluoromethyl)-2-(1,1,1,3,3,3-hexafluoroisopropyl)-4-(2,2,2-trifluoroethylidene)cyclobutene (6). Procedure A. Triethylamine (1.72 g, 2.25 mL, 16.9 mmol) was added to a stirred solution of hydrazone **1**[1,3] (2.65 g, 8.49 mmol) in dry acetonitrile (10 mL) under N_2 at room temperature. The solution was stirred at 80 °C for 3 h. After cooling, the reaction mixture was dissolved in methylene chloride (50 mL) and washed with cold 2 N HCl solution (2 × 50 mL) and then with water (50 mL). Analysis by ^{19}F NMR revealed that the major product was the volatile vinyl fluoride **11** (yield: 1.72 g, 76%). ^{19}F NMR (CD_3CN): δ −65.3 (s, *gem* CF_3, 6F), −71.4 (s, vinyl CF_3, 3F), −122.5 (d, J = 30 Hz, vinyl F, 1F). ^{1}H NMR (CD_3CN): δ 4.76 (m, isopropyl H, 1H), 6.06 (dd, vinyl H, J_{HH} = 10.5 Hz, J_{HF} = 30 Hz, 1H). GC/MS: 264 (M^+). The yield of methylenecyclobutene **6** in the methylene chloride solution was 0.44 g (21%) by NMR. In another run, after the reaction mixture was cooled to room temperature, volatiles were evaporated at 10 Torr and room temperature. Concentrated sulfuric acid (0.9 mL, 17 mmol) was added to the residue. With stirring, the resulting mixture was subjected to vacuum transfer at ∼50 mTorr. The methylenecyclobutene was caught in a liquid N_2 trap and, following a second vacuum transfer, was further purified by preparative GC. Bp 136 °C. IR (neat): 1272, 1135, 983, 755, 690, 601, 494 cm^{-1}. ^{1}H NMR (CD_3CN): δ 6.39 (q, J = 8 Hz, vinyl H, 1H), 5.14 (septet, J = 8.5 Hz, isopropyl H, 1H). ^{19}F NMR (CD_3CN): δ −58.3 (broad s, vinyl CH*C*F_3, 3F) −61.5 (broad s, isopropyl CF_3, 6F), −63.3 (broad s, ring vinyl CF_3, 3F), −65.0 (broad s, ring *gem* CF_3, 6F). GC/MS (*m*/*z*): 488 (M^+). ^{13}C NMR (acetone-d_6), F decoupled: δ 147.6, 138.4, 130.5 (C1, C2, C4), 121.5, 121.4, 121.1, 116.9 (CF_3), 115.7 (d, J_{CH} = 174 Hz, vinyl CH), 62.4 (C3), 47.9 (d, J_{CH} = 135 Hz). $Cr(OAc)_3$ was added to make very weak ^{13}C signals detectable by shortening relaxation times.

Procedure B. Dry triethylamine (0.20 mL, 1.48 mmol) was added under nitrogen at 0 °C to a stirred solution of acetylene **12** (0.720 g, 2.95 mmol) in dry CH_3CN in a septum-stoppered round-bottom flask. Stirring was continued for 20 min at 0 °C, and then the solution was allowed to warm slowly to room temperature. Additional triethylamine (0.20 mL, 1.48 mmol) was added with stirring. By ^{19}F NMR, with hexafluorobenzene as the internal standard, the yield of methylenecyclobutene **6** as its anion was 72%. Volatiles were evaporated at 10 Torr and room temperature. Concentrated sulfuric acid (0.5 mL) was added to the residue, and the well-stirred mixture was subjected to vacuum transfer at ∼50 mTorr. The product, caught in a liquid N_2 trap, was a mixture of **6** with lesser amounts of other isomers of MW 488 (70% yield). Separation by preparative GC gave much purer **6**, but other isomers were not eliminated completely.

(*Z*)-1,3,3-Tris(trifluoromethyl)-2-(1,1,1,3,3,3-hexafluoroisopropyl)-4-(2,2,2-trifluoroethylidene)cyclobutene (7). To allene **15** in CD_3CN in an NMR tube at −44 °C was added 0.5 equiv of triethylamine. ^{19}F NMR and ^{1}H NMR spectra were recorded at that temperature. ^{19}F NMR (CD_3CN) for anion **17**: δ −51.0 (broad s, vinyl CH*C*F_3, 3F), −52.6 (broad s, isopropyl CF_3, 3F), −54.1 (s, isopropyl CF_3, 3F), −58.5 (broad s, ring vinyl CF_3, 3F) −63.6 (broad s, ring *gem* CF_3, 6F). ^{1}H NMR (CD_3CN): 4.75 (q, vinyl H, J = 10 Hz, 1H). As the temperature was gradually brought to room temperature while monitoring NMR signals, **17** was transformed completely into anion **18**. ^{19}F NMR (CD_3CN): δ −50.6 (m vinyl CH*C*F_3, 3F), −54.0 (m, isopropyl CF_3, 3F), −54.1 (m, isopropyl CF_3, 3F), −58.8 (m, ring vinyl CF_3), −64.2 (m, *gem* CF_3, 6F). ^{1}H NMR (CD_3CN): 4.63 (s, J = 9 Hz, vinyl H, 1H). When a solution of **17** was prepared as described above and quenched with acid at −44 °C, both methylenecyclobutenes **6** and **7** were formed. The mixture was warmed to room temperature. ^{19}F NMR (CD_3CN) for **7**: δ −59.9 (m, CH*C*F_3, 3F), −63.1 (m, isopropyl CF_3, 6F), −63.3 (m, ring vinyl CF_3, 3F), −66.0 (m, *gem* CF_3, 6F). ^{1}H NMR (CD_3CN) for **7**: δ 6.48 (q, J = 8.0 Hz, vinyl H, 1H), 5.25 (m, isopropyl H, 1H).

Perfluoro-4-methyl-2,3-pentanedione Bishydrazone 14.[6] Hydrazine hydrate (13.0 g, 271 mmol) was added dropwise during 1 h to a stirred solution of perfluoro-4-methyl-2-pentene (**13**) (20.0 g, 66.7 mmol) in 1,2-dimethoxyethane (60 mL). Stirring was continued for 3 days at room temperature. Volatiles were removed from the resulting homogeneous solution at 50−100 Torr and room temperature. The residue was dissolved in ether (100 mL) and washed with water (2 × 75 mL). After drying over Na_2SO_4, the ether solution was stripped on a rotary evaporator. Vacuum distillation of the residue at 1 Torr gave bishydrazone with bp 87−89 °C. [Caution: excessive heat leads to decomposition of the product.] Yield: 15.80 g, 78%. Mp 84 °C. ^{1}H NMR ($CDCl_3$): δ 6−7 (broad singlets, NH_2, 2H), 6.13 (broad, NH_2, 2H), 3.91 (septet, J = 7.5 Hz, isopropyl H, 1H). ^{19}F NMR δ (−63.9, *gem* CF_3, 6F), −66.3 (m, CF_3, 3F). GC/MS (*m*/*z*): 304 (M^+).

***4H*-Perfluoro-4-methyl-2-pentyne (12) and *4H*-Perfluoro-2-methyl-2,3-pentadiene (15).**[6] Powdered mercuric acetate (4.61 g, 14.5 mmol) was placed in a 3-necked flask fitted with a mechanical stirrer, solids addition funnel, and connection to a liquid N_2 trap. Perfluoro-4-methyl-2,3-pentanedione bishydrazone **14** (2.20 g, 7.23 mmol) was added with stirring from the funnel during 30 min, as volatile products collected in the trap. Stirring was continued at room temperature for 1 h, then the mixture was heated at 100 °C. After a total reaction time of 3 h, the trapped product was subjected to bulb-to-bulb distillation. The distillate contained a mixture of acetylene **12** and allene **15** in the ratio 1:1.4, respectively. Yield: 0.84 g, 48%. Bp 50−52 °C. ^{19}F NMR ($CDCl_3$) for **12**: δ −52.4 (s, acetylenic CF_3, 3F), −66.6 (s, *gem* CF_3, 6F); for **15**: δ −60.7 (s, CH*C*F_3, 3F), −61.5 (s, *gem* CF_3, 6F). ^{1}H NMR ($CDCl_3$): 6.49 (m, allene H, 1H), 4.10 (m, acetylene H, 1H). The acetylene slowly isomerized to the allene upon standing at room temperature, and when a mixture of the two was dissolved in acetonitrile, the acetylene isomerized to the allene immediately and completely.

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Supporting Information Available: *Z* matrices and total energies at the B3LYP/6-31G* level of theory for methylenecyclobutene rotamers **6a** and **6b** and for anions **17** and **18**; also ^{1}H, ^{13}C, ^{19}F NMR and (F, H) NOESY spectra of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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