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Ambiphilic Properties of $SF_5CF_2CF_2Br$ Derived Perfluorinated Radical in Addition Reactions Across Carbon−Carbon Double Bonds

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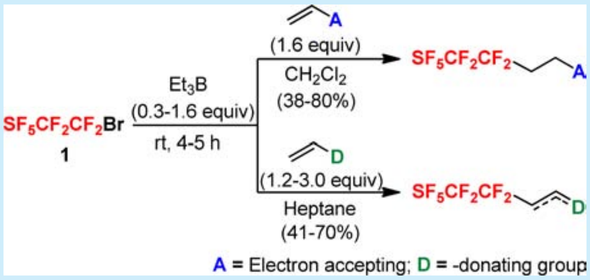
Supporting Information

ABSTRACT: The extraordinary properties of the pentafluorosulfanyl (SF_5) group attract attention of organic chemists. While numerous SF_5-substituted compounds have been synthesized, the direct introduction of $SF_5(CF_2)_n$ moieties has remained almost unexplored. Our investigations revealed the ambiphilic character of the $SF_5CF_2CF_2$ radical. Addition reactions to electron-rich or electron-deficient alkenes profit either from its electrophilic or nucleophilic properties. Thus, the readily available $SF_5CF_2CF_2Br$ proved to be a promising and versatile building block for the introduction of this perfluorinated moiety.



Incorporation of a fluorine atom or fluorinated groups into organic molecules often results in beneficial changes in their physicochemical and biochemical properties.[1] This realization has led to a rapid development of safe and convenient fluorination and trifluoromethylation methods.[2] Nevertheless, other perfluorinated substituents have also begun to attract increasingly more attention of organic chemists.[3] Among them, the pentafluorosulfanyl group (SF_5) deserves special attention.[4] The most convenient method of introducing this highly lipophilic, bulky and strongly electron-withdrawing substituent into aliphatic compounds involves a radical addition of pentafluorosulfanyl halide (SF_5X, where X = Cl or Br) across multiple bonds.[5] Aromatic derivatives, however, can be synthesized via oxidative fluorination of the corresponding thiols or disulfides, particularly according to the recent advances by Umemoto.[6] These chemistries have been well explored leading to syntheses of various SF_5-containing compounds such as peptides,[7] antimalarial agents,[8] and liquid crystals.[9] The direct introduction of $SF_5(CF_2)_n$ moieties, however, has remained almost unexplored. Recently, we published the use of $SF_5CF_2C(O)Cl$ as a versatile building block.[10] Earlier $SF_5CF_2CF_2I$[11] was used for perfluoroalkylation of benzene[12] and chain-extension reactions leading to higher perfluorocarbon and partially fluorinated hydrocarbon derivatives.[11b,13] In this report we present results from an investigation of the reactivity of $SF_5CF_2CF_2Br$ **1** in radical reactions with electronically different alkenes. Compared to its iodine analogue, **1** is more easily accessible by addition of SF_5Br to tetrafluoroethylene (TFE).[14]

Because of the σ electron withdrawing effect of the fluorine atom, perfluorinated radicals show electrophilic properties.[15] Therefore, we decided to initially investigate electron-rich alkenes such as enol ethers as potential reaction partners using triethylborane (Et_3B) as a radical initiator in heptane.

$SF_5CF_2CF_2Br$ **1** reacted with ethyl vinyl ether and 2-methoxy propene leading to aldehyde **2a** and ketone **2b**, respectively. These volatile products were immediately converted to their phenylhydrazones **2a′** and **2b′** using crude materials, in order to determine the yields and further ensure the structures of the formed products.[16] The reaction with 2,3-dihydrofuran, in turn, resulted in the direct formation of **2c**, which was converted in situ to its isopropyl acetal **2c′** in order to facilitate isolation. Similarly, tetrahydropyran gave the 3-substituted product **2d** in 61% isolated yield (Scheme 1).

The reactions of ethyl prop-1-en-1-yl and but-1-en-1-yl ethers with $SF_5CF_2CF_2Br$ **1** were complete after 4 h giving mixtures of products, which could not be separated. Treatment of the crude products with 2,4-dinitrophenylhydrazine under the aforementioned conditions gave minor amounts of several fluorinated products.

For the reaction of bromide **1** with ethyl vinyl ether (molar ratio 1:1.2), the polarity of the solvent was important. The aldehyde **2a** was formed as a major product in heptane (after hydrolysis), along with minor amounts of the corresponding diethyl acetal **3** (ratio 4:1). Executing the same reaction in CH_2Cl_2 resulted in the preferred formation of the acetal **3** (ratio 1.0:1.5). Under these conditions, incomplete consumption of the bromide **1** was observed, while no ethyl vinyl ether remained in the crude reaction mixture (^1H NMR). In the presence of 3 equiv of ethyl vinyl ether, bromide **1** was fully converted, and **3** was

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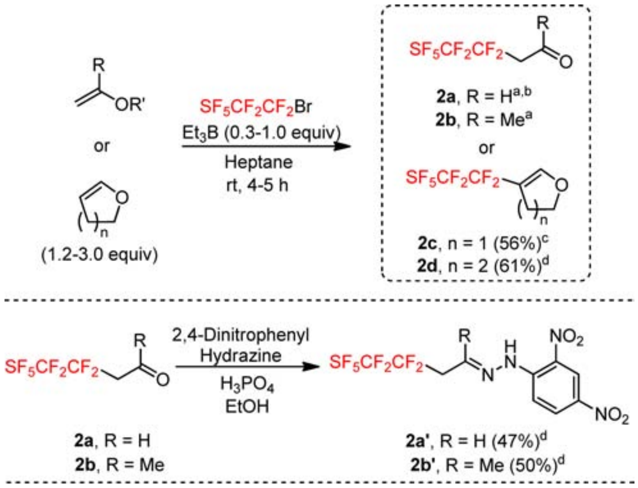
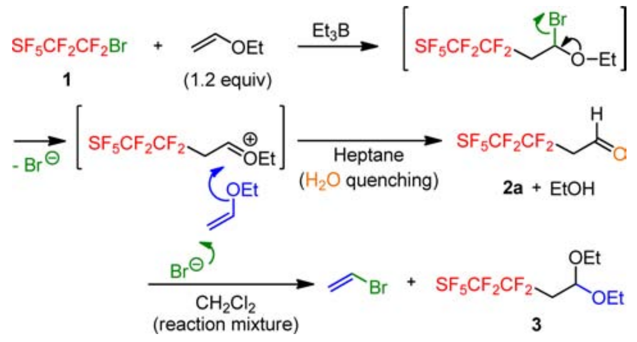
Scheme 1. Reactions with Enol Ethers and Formation of Hydrazones from the Formed Volatile Ketones



[a]Isolated as 2,4-dinitrophenyl hydrazones **2a′** or **2b′**. [b]Isolated as 4:1 mixture with its diethyl acetal **6** (^{19}F NMR and ^{1}H NMR). [c]Isolated yield of the corresponding isopropyl acetal **2c′**. [d]Isolated yield.

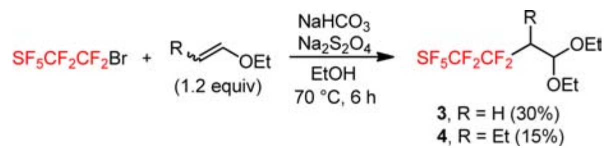
isolated exclusively (42% yield). The mechanism[17] depicted in Scheme 2 provides a plausible explanation for the findings.

Scheme 2. Solvent-Dependent Reaction with Ethyl Vinyl Ether



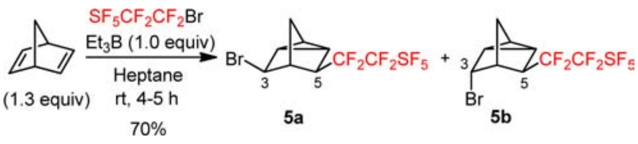
Direct acetal formation can be accomplished by running the reaction in ethanol in the presence of sodium dithionite ($Na_2S_2O_4$) as a radical initiator (Scheme 3).[18] However, the acetals **3** and **4** were isolated in low yields.

Scheme 3. Sodium Dithionite Initiated Reactions in Ethanol



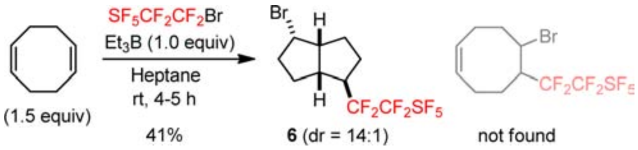
These results encouraged us to investigate reactions of reactive dienes. Under the established conditions norbornadiene underwent transannular π-cyclization,[19] and a 5:6 mixture of products **5a** and **5b** was isolated in 70% yield (Scheme 4). According to the literature, proton signals H−C5 for *endo*-3-halogen and *exo*-5-substituted nortricyclanes are shifted more downfield in comparison to their *exo*-3-halogen and *exo*-5-substituted counterparts.[20] Therefore, the signals at 2.35 and 3.16 ppm in the ^{1}H NMR spectrum of the mixture were assigned to H−C5 for **5a** and **5b**, respectively. Moreover, it is also known that the H−C3 signals for halogenated nortricyclanes appear with characteristic shifts at approximately 4.00 ppm.[20c] Hence, 3.96 and 4.00 ppm signals were assigned to **5a** and **5b**, respectively, which are consistent with the chemical shifts and integrations of the H−C5 signals.

Scheme 4. Transannular π-Cyclization Reaction of Norbornadiene



The reaction with (*Z*,*Z*)-cycloocta-1,5-diene, in contrast to the reported addition of SF_5Cl,[20c] gave no 1,2-addition product but exclusively the transannular π-cyclization product **6** (dr = 14:1), based on NMR spectroscopy (Scheme 5). Incomplete conversion of the starting bromide, however, resulted in lower isolated yield (41%), which could not be improved by the addition of larger amounts of Et_3B and/or the diene.

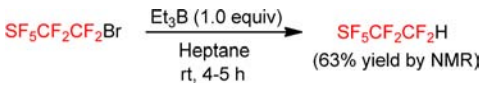
Scheme 5. Transannular π-Cyclization Reaction of (*Z*,*Z*)-Cycloocta-1,5-diene



At this point, it has to be mentioned that ordinary alkenes, such as dec-1-ene, cyclohexene, cycloheptene, and norbornene, as well as diallyl ether, and vinyl- or allyl acetate, did not react with the bromide **1** under the aforementioned conditions. 2,5-Dihydrofuran showed low conversion; *p*-methoxystyrene after low conversion gave a complex mixture of products (NMR), while the *p*-CF_3 analogue did not react. Treatment of allyl acetate with **1** under UV-irradiation and by initiation with $S_2O_4^{2-}$ or dibenzoyl peroxide gave complex product mixtures. To the best of our knowledge, there is no derivative chemistry known for $CF_3CF_2CF_2Br$. In contrast, addition reactions of $CF_3CF_2CF_2I$ to a large variety of alkenes, such as different 1-alkenes, cycloalkenes, α,ω-dienes including norbornadiene as well as allyl- and vinyl acetates, were reported to give addition products in moderate to good yields.[21] Similar reactions with allyl ethers and specifically substituted allyl alcohols and allyl amines were reported to be low yielding and unselective.[22]

Interestingly, the reaction of **1** with 1,3,5-trimethoxybenzene, another electron-rich system, resulted in the formation of $SF_5CF_2CF_2H$[23] as the major product. No bromoaryl derivatives were found. In order to ensure that 1,3,5-trimethoxybenzene was not the source of the hydrogen atom, we conducted a control experiment using Et_3B alone. $SF_5CF_2CF_2H$ was formed in 63% NMR yield (Scheme 6).

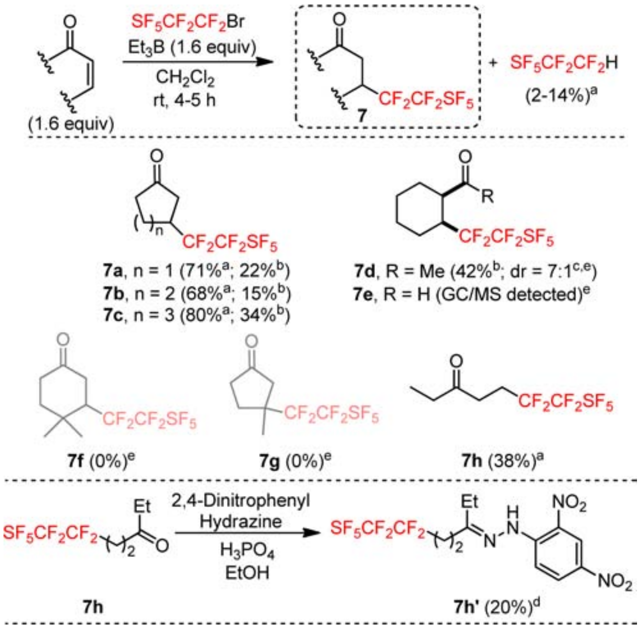
Scheme 6. Control Experiment Using Et_3B Alone Leading to $SF_5CF_2CF_2H$ Formation



These findings suggest that (under the conditions used) quickly reacting partners are necessary to trap the $SF_5CF_2CF_2$ radical and to prevent the formation of $SF_5CF_2CF_2H$ from Et_3B or the solvent. The formation of $SF_5CF_2CF_2H$ was never detected in reactions of enol ethers or the aforementioned dienes.

Our further investigations focused on the radical conjugate addition of **1** to α,β-unsaturated ketones (Scheme 7).[24] We speculated that the π-donating effect of fluorine would create a partial nucleophilic character of the perfluorinated radical. Again, Et_3B was used as a radical initiator and a Lewis acid.[25]

Scheme 7. Radical Conjugate Addition Reactions and Conversion of the Ketone 7h to Its Hydrazine 7h′



[a] Yields determined by ^{19}F NMR spectroscopy (*m*-fluorotoluene as an internal standard). [b] Isolated yields. [c] Determined by ^{1}H NMR spectroscopy. [d] Isolated yield based on ethyl vinyl ketone. [e] Amount of $SF_5CF_2CF_2H$ formed was not determined.

A model reaction with 2-cyclohexen-1-one in CH_2Cl_2 resulted in full conversion of the starting material yielding the desired addition product **7b** and minor amounts of $SF_5CF_2CF_2H$ (reactions in THF and hexane led to formation of $SF_5CF_2CF_2H$ as the major product). Moreover, the addition product of ethyl radical derived from Et_3B was also observed. The high volatility of **7b** resulted in low isolated yield of 15% in comparison to 69% determined by ^{19}F NMR spectroscopy of the crude reaction mixture. Similar yields were obtained with 2-cyclopenten-1-one and 2-cyclohepten-1-one, which gave products **7a** (71% by NMR and 22% isolated yields) and **7c** (80% NMR and 34% isolated yields), respectively. The reaction with 1-acetyl-cyclohex-1-ene, in turn, gave the less volatile addition product **7d** as an inseparable mixture of cis and trans isomers in a 7:1 ratio (42% isolated yield due to incomplete consumption of **1**). Unfortunately, the closely related 1-cyclohexene-1-carboxaldehyde did not react sufficiently, and the desired product **7e** could only be detected with GC/MS analysis. Reactions with 4,4-dimethyl-2-cyclohexen-1-one and 3-methyl-2-cyclopeten-1-one to form **7f** and **7g** could not be realized probably due to steric reasons. Finally, a reaction with ethyl vinyl ketone gave a low yield of volatile product **7h**, which could not be isolated. Therefore, the crude reaction mixture was treated with an EtOH/sat. H_3PO_4 (2:3) solution of 2,4-dinitrophenylhydrazine to give the corresponding hydrazone **7h′** in 20% yield. The low yield is a result of a significant formation of $SF_5CF_2CF_2H$ (14%, ^{19}F NMR spectroscopy) and a competing radical conjugate addition reaction of ethyl vinyl ketone with ethyl radicals derived from Et_3B. The corresponding hydrazone **7h″** (see SI) of the addition product was isolated in 49% yield based on ethyl vinyl ketone. To the best of our knowledge, reactions of $CF_3CF_2CF_2I$ with α,β-unsaturated ketones have not been described, while corresponding reactions with acrylates have been investigated.[21]

Finally, we conducted a qualitative competition experiment with an electron-rich and an electron-deficient alkene in order to get information on the relative electrophilic or nucleophilic character of the radical. $SF_5CF_2CF_2Br$ (1.0 equiv) was dissolved in CH_2Cl_2 along with dihydropyran and 2-cyclohexen-1-one (2.0 equiv each), and Et_3B (1.6 equiv) was added dropwise. Only dihydropyran reacted yielding 75% (NMR) of **1d**. As expected, the electrophilic properties of the $SF_5CF_2CF_2$ radical predominate, which was also found for the $CF_3CF_2CF_2$ radical.[26]

In summary, our investigations of the reactivity of $SF_5CF_2CF_2Br$ demonstrate the ambiphilic character of the derived perfluoroalkyl radical. It is noteworthy that bromide **1** reacts readily with alkenes containing either electron-donating or electron-accepting substituents, while ordinary and electron-poor alkenes are inferior reaction partners. These findings can be explained by different stabilizing effects of the substituents on the intermediate radicals (Figure 1).

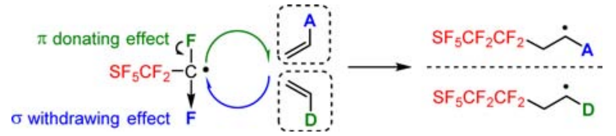


Figure 1. Ambiphilic properties of $SF_5CF_2CF_2Br$ derived perfluorinated radical. Stabilization of the intermediate radicals through electron-accepting (A) and electron-donating (D) groups.

In conclusion, $SF_5CF_2CF_2Br$ proved to be a promising and versatile starting material for introduction of the new perfluorinated moiety providing potential building blocks for pharmaceuticals and agrochemicals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, full spectroscopic data, and copies of the ^{1}H, ^{13}C, and ^{19}F NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Konrad Seppelt on the occasion of his 70th birthday.

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