

Chlorination of Perchloro-1,3-butadiene and Perchlorocyclopentadiene with Cl₂/SbF₅/SO₂ClF at -78 °C to Their Stable Perchloroallylic Cations¹

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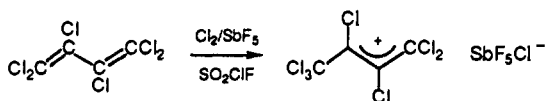
Abstract: Chlorination of perchloro-1,3-butadiene and perchlorocyclopentadiene, highly unreactive dienes, takes place quantitatively with Cl₂/SbF₅ in SO₂ClF solution at -78 °C, giving the corresponding perchloroallylic cations. As highly deactivated perchlorinated dienes generally do not undergo electrophilic reactions and SbF₅ itself does not oxidize these dienes, the unusual reactivity is best explained by oxidation of Cl₂ by SbF₅ to Cl₂^{•+} followed by single electron transfer (SET) from the perchlorodienes, giving the corresponding allylic radical cations. Chlorine quenching of the radical cations forms the perchloroallylic cations.

Lewis acid halide catalyzed electrophilic chlorination of aromatics is an essential part of chemistry for over a century.² Electrophilic halogenation of alkenes and alkynes is similarly widely used.³ Olah et al. in the 1970s first explored electrophilic halogenation of alkanes.⁴ SbF₅-catalyzed chlorination of even methane was effected in SO₂ClF solution at low temperature. At the same time Wassermann et al. observed that liquid Cl₂ in excess SbF₅ provides a powerful oxidant that was able to generate the hexachlorobenzene dication.⁵ Subsequently, Gillespie and Morton,⁶ Symons,⁷ and Eachus⁸ investigated liquid Cl₂ in various superacidic media at different temperatures and found no evidence by EPR studies for possible formation of Cl⁺ or Cl₂^{•+}. As was pointed out,^{8,9} even if either species had formed, it would not have been discernible by ESR experiments due to their intrinsic electronic properties (efficient spin relaxation, unquenched orbital magnetism owing to orbital degeneracy of the π* electron, very large anisotropy). However, molecular chlorine in superacids due to the presence of oxygen impurities did yield ESR absorptions corresponding to Cl₂O^{•+}, ClO^{•+} radical cations.

Results and Discussion

We now report our studies of surprisingly effective and facile chlorination of the heretofore generally unreactive perchloro-1,3-butadiene and perchlorocyclopentadiene with Cl₂ in SO₂ClF solution at -78 °C, giving the corresponding perchloroallylic cations.

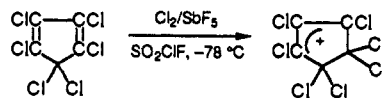
When perchlorobuta-1,3-diene is reacted with a solution of chlorine in 4-5-fold excess of SbF₅ with SO₂ClF as solvent at -78 °C the perchloro-1-methylallyl cation is cleanly formed. The ¹³C NMR of the resulting solution exhibits four resonances of equal intensity at δ(¹³C) 213.2, 188.4, 142.7, and 94.5.



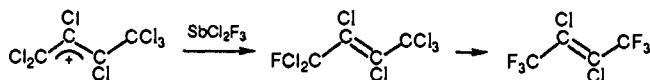
Interestingly perchlorobutadiene has been reported to react with a mixture SbF₅ and Cl₂ in an autoclave at 155 °C to give CF₃-CCl=CClCF₃.^{8b} This reaction may, although not recognized until

now, be related to the presently reported study, with intermediately formed weaker SbF₃Cl₂ requiring harsher reaction conditions and the perchloro-1-methylallyl cation undergoing Swarts-type fluorine-exchange reaction.

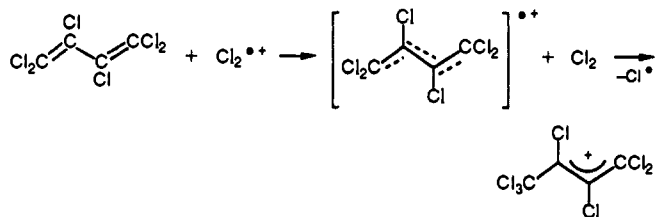
Perchlorocyclopentadiene when reacted with Cl₂-SbF₅ in SO₂ClF under similar conditions at -78 °C clearly gave the corresponding perchlorinated allylic cation.



Perchlorobutadiene was previously considered to be extremely unreactive.^{8a} It was also found inert toward SbF₅/SO₂ClF in the absence of Cl₂. It does not add Cl₂ in light and withstands polymerization at pressures as high as 100 atm.^{8a} Electrophilic addition of the polarized δ⁺Cl₂ → δ⁻SbF₅ complex to the diene, although possible, seems less probable due to lack of sufficient π-electron donor ability of the highly deactivated perchlorinated diene.



Alternatively and more probably, the chlorination reaction of perchlorobuta-1,3-diene and perchlorocyclopentadiene can be considered to involve initial single electron transfer (SET) from the dienes to Cl₂^{•+} formed by oxidation of liquid chlorine by excess SbF₅ in SO₂ClF solution. The formed dieny radical cation is then immediately quenched by chlorine.



Houk and Olah⁹ have studied the singlet-triplet gap of halogen cations such as X⁺, X₂^{•+}, X₂H⁺, etc., by ab initio calculations and found that for the monoatomic halogen cations (X = F, Cl), the triplet state is substantially favored (i.e. 60 kcal/mol for F⁺ and 35 kcal/mol for Cl⁺). When comparing the ground-state energies of the doublet halogen radical cations F₂^{•+} and Cl₂^{•+} relative to their respective parent neutral molecules, F₂ and Cl₂, they calculated ionization potentials of 258 kcal/mol for Cl₂ → Cl₂^{•+} + e⁻ and 354 kcal/mol for F₂ → F₂^{•+} + e⁻. These calculations are in reasonable accord with the experimental results of 265.0 for Cl₂^{•+} and 362.0 for F₂^{•+}.⁵ Even if the computational data only relate to the gas phase, the general trend must hold for the solution phase as well. This explains why in ordinary solution chemistry neither Cl₂^{•+} nor F₂^{•+} has been detected. In the case of F₂^{•+}, the

(1) Electrophilic Reactions at Multiple Bonds. 4. For part 3, see: Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1845.

(2) For a comprehensive review, see: Braendlin, H. P.; McBein, E. T. *Friedel Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1964; Part 2, p 1517.

(3) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, *94*, 6864.

(4) Olah, G. A.; Renner, R.; Schilling, P.; Mo, Y. T. *J. Am. Chem. Soc.* **1973**, *95*, 7680.

(5) Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Chandross, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 1965.

(6) Gillespie, R. J.; Morton, M. J. *Inorg. Chem.* **1972**, *11*, 591.

(7) Symons, M. C. R.; Eachus, R. S. *J. Chem. Soc., Dalton Trans.* **1976**, 431.

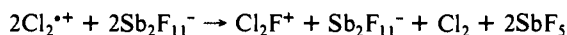
(8) (a) Henne, A. L.; Trott, P. *J. Am. Chem. Soc.* **1947**, *69*, 1820. (b) Fruhwirth *Ber. Dtsch. Chem. Ges.* **1941**, *74*, 1700.

(9) Li, Y.; Wang, X.; Jensen, F.; Houk, K. N.; Olah, G. A. *J. Am. Chem. Soc.*, following paper in this issue.

energetics appear too unfavorable to be able to even invoke a possible intermediacy of this species. With Cl_2^{*+} , however, the energetics are more favorable assuming that a powerful enough oxidant is employed. As discussed Cl_2 in excess SbF_5 was recognized to be a powerful oxidizing system.

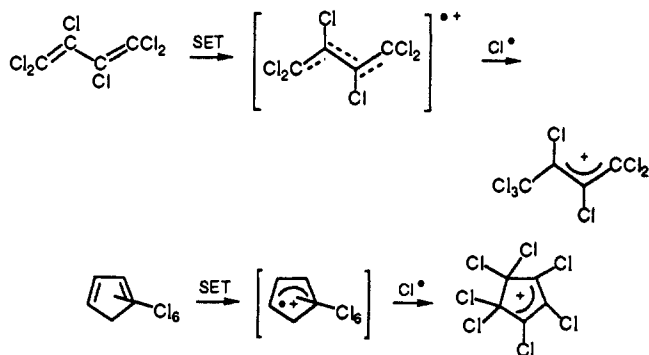
In order to rule out involvement of Cl_2O^{*+} (or ClOF^{*+}), which can be formed if any oxygen is present in the system,¹⁰ we undertook EPR studies of solutions of Cl_2 in excess SbF_5 and SO_2ClF . These solutions displayed broad absorptions at -80°C , but their intensities were low, since they are caused by trace contamination of oxygen in the medium.^{6,7} If Cl_2O^{*+} radical cation impurity was the electrophile, side reactions after its consumption would have occurred, or at least unreacted starting material would have been present, neither of which was observed. The data therefore are in accord that Cl_2^{*+} could be generated in situ in the superacidic medium in the presence of oxidizable substrates. Cl_2^{*+} is extremely reactive and (vide supra) abstracts a single electron even from deactivated π -systems such as perchloro-1,3-butadiene.

As Gillespie and Morton¹⁰ pointed out, Br_2^{*+} and I_2^{*+} can only be observed in solvents in which the corresponding Br_3^+ and I_3^+ cations are stable to disproportionation. The Cl_2^{*+} cation is therefore also predicted to undergo disproportionation according to

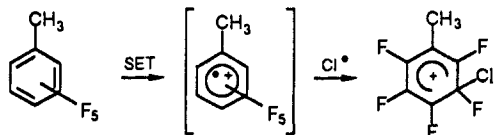


with a negative ΔH of reaction¹⁰ due to the high Cl-F bond energy. Since the Cl_3^+ cation only exists as solid salt at low temperatures, -76°C ,¹¹ and undergoes disproportionation upon dissolution in strong superacid, the possibility of detecting the Cl_2^{*+} radical cation in solution is very low. Similar attempts to prepare Xe^+ cation always resulted in formation of XeF^+ as the product.¹²

Based on the foregoing it is suggested that Cl_2^{*+} is intermediately generated $\text{SbF}_5/\text{SO}_2\text{ClF}$ solution as a highly reactive species. SET from the perchlorodienes is then followed by quenching of the radical cations by chlorine, giving the perchloroallylic cations as the sole stable, observable product.



It should also be mentioned that $\text{Cl}_2/\text{SbF}_5/\text{SO}_2\text{ClF}$ forms from pentafluorotoluene, as observed first by Dobronravov and Shteingarts,¹³ the 1-chloro-3-methylpentafluorobenzenium ion. It was considered by authors that the product is formed by electrophilic chlorine-cation addition to the aromatic ring. However, due to the highly deactivated nature of the perfluoro-arene initial SET by Cl_2^{*+} seems again more probable.



Further indication for SET is the observation that when reacting aromatics (naphthalene, anthracene, diphenylacetylene) with

(10) Gillespie, R. J.; Morton, M. J. *Q. Rev. Chem. Soc.* **1971**, 553.

(11) Gillespie, R. J.; Morton, M. J. *Inorg. Chem.* **1970**, 9, 811.

(12) McRae, V. M.; Peacock, R. D.; Russel, D. R. *Chem. Comm.* **1969**, 62.

(13) Shteingarts, V. D.; Dobronravov, P. N. *Zh. Org. Khim.* **1976**, 12, 2005.

Cl_2/SbF_5 in SO_2ClF at -78°C initially strong EPR signals are observed, with lack of any observable NMR resonance, prior to chlorination taking place.

Finally it should be mentioned that the de facto reagent could also be Cl^+ , since the monoatomic chlorine cation on the basis of theoretical calculations would have a preferred triplet rather than singlet state.⁹ It therefore could react in the same manner, i.e. via fast SET with the perchlorinated dienes and followed subsequent quenching by Cl_2 . Due to its elusiveness even in the gas phase, there is so far, however, no indication that monoatomic chlorine cation could be the de facto electrophile.

In conclusion, solutions of Cl_2/SbF_5 (excess) in SO_2ClF are capable of chlorinating otherwise unreactive perchlorinated dienes to their respective perchlorinated stable allylic cations. This remarkable new chlorination reaction is considered to involve initial SET by Cl_2^{*+} from the perchlorinated dienes.

Experimental Section

NMR Spectroscopy. ^{13}C spectra were recorded on either a Varian Associates Model FT 80 (external lock) or Varian Associates Model VXR 200 (data system VXR 4000) NMR spectrometer equipped with a 10-mm and 5-mm broad-band variable-temperature probe, respectively. ^{13}C resonances were referenced to external (capillary) tetramethylsilane.

The peak assignments are based on decoupling experiments, J -modulated spin-echo techniques and comparison with closely related analogous known compounds. Multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, with coupling constants in parentheses, following the convention denoting the coupling nuclei as subscript and the bond distances as superscript.

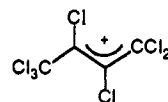
EPR Spectroscopy. EPR spectra were recorded on an IBM/Brucker ER 200 D EPR spectrometer equipped with a variable temperature unit ER 4111 VT.

Chemicals. Hexachlorobuta-1,3-diene, perchlorocyclopentadiene, pentafluorotoluene, SO_2ClF , and Cl_2 (gas) were commercially available (Aldrich/Columbia Organic Chemicals/Matheson). SbF_5 (Ozark-Mahoning) was distilled twice in an all glass apparatus prior to use.

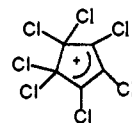
Chlorination of Perchlorinated Dienes with Cl_2/SbF_5 in SO_2ClF . Typically 0.05 mL of Cl_2 was condensed into an oven-dried NMR tube charged with Ar and precooled to -78°C in a dry ice/acetone slush. Approximately 0.05 mL of SO_2ClF was added by a precooled pipet, and the solution was vortex mixed to ensure efficient mixing. Then, 0.3 mL of a 2:1 mixture of SbF_5 and SO_2ClF was transferred into the NMR tube and vortex mixed until a clear yellow solution resulted and again placed into the cooling bath. Finally, a precooled 1:1 solution or suspension of the perchlorinated diene and SO_2ClF (0.1 mL total volume) was pipetted into the NMR tube and vortexed with intermittent cooling to -78°C , whereupon a clear, colored solution was obtained. The tube was then inserted into the precooled probe of the NMR spectrometer.

The sample preparation for EPR measurements was identical with that described for the NMR recordings.

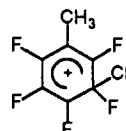
^{13}C Data of Cations:



94.5 (CCl_3), 213.2 ($\text{Cl}_3\text{C}\text{CCl}$), 142.7 ($\text{Cl}_2\text{C}\text{CCl}$), 188.4 (Cl_2CC)



82.7 (C_1), 213.9 (C_3), 134.1 (C_2)



4.7 (CH_3), 117.7 (CCH_3), 89.8 (CClF), 136.5 (ClFCCFCCH_3), 162.7 (ClFCCFCF), 180.6 (ClFCCFCF), 199.3 ($\text{ClFCCFCCH}_3\text{CF}$)

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Registry No. Perchloro-1,3-butadiene, 87-68-3; perchlorocyclopentadiene, 77-47-4.