
Unexpected Reactions of (Heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) Hexafluoroarsenate with Sodium Fluoride and Antimony Pentafluoride

Hermann J. Frohn^{*a} and Vadim V. Bardin^b

^a *Fachgebiet Anorganische Chemie, Gerhard-Mercator-Universität Duisburg, D-47048 Duisburg, Germany.*

Fax: +49 203 379 2231; e-mail: hi271fr@unidui.uni-duisburg.de

^b *Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation.*

The reactivity of (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) hexafluoroarsenate **1** towards a fluoride donor and acceptor has been investigated; the interaction of **1** with NaF led to perfluoro-3-methylenecyclopentene and xenon. No dication $[\text{C}_6\text{F}_6\text{Xe}]^{2+}$ was detected by ^{19}F NMR spectroscopy when $[\text{1-Xe}^+-1,4\text{-C}_6\text{F}_7][\text{AsF}_6]^-$ was treated with $\text{SbF}_5\text{-SO}_2$, $\text{SbF}_5\text{-SO}_2\text{FCl}$ or neat SbF_5 .

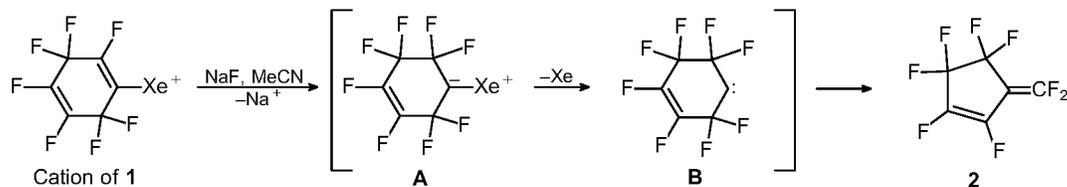
We recently reported the first preparation of the alkenylxenon(II) salts (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) **1** and (nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenates.¹ Both cations were characterized by ^{13}C , ^{19}F and ^{129}Xe NMR spectroscopy and by their conversions into the cycloolefines 1-R-1,4-C₆F₇ or 1-R-C₆F₉ (R = Br, Ph) when

they were treated with the bromide anion or benzene, respectively. In both cases replacement of the xenon atom for the halogen atom or the aryl group proceeded in a similar manner to that described for pentafluorophenylxenon(II) hexafluoroarsenate.^{2,3} In contrast to the above pattern of reactivity the interaction of $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ with the fluoride

anion ("hardest" nucleophile) in MeCN led to the formation of C_6F_5H and $C_6F_5-C_6F_5$.² In the course of our investigations into organoxenon(II) derivatives we studied the interaction of compound **1** with the fluoride donor NaF as well as with the fluoride acceptor antimony pentafluoride.

Surprisingly, the interaction of diene **1** with sodium fluoride in MeCN under heterogeneous conditions resulted in the formation of perfluoro-3-methylenecyclopentene **2** accompanied by xenon evolution. Olefine **2** was the major component of the reaction mixture and was unambiguously identified by ^{19}F NMR spectroscopy.⁴ Minor components were not analysed in detail, but octafluorocyclohexadienes, hydrogen-containing heptafluorocyclohexadienes or perfluorinated bi(hexadienyls) were not found.[†]

The unexpected conversion of the dienyl xenonium cation in salt **1** to cyclopentene **2** may be rationalised by assuming a preferential attack of the "hard" anionic nucleophile fluoride at the "hard" electrophilic centre C(2), rather than at the "soft" electrophilic centre xenon(II). The neutral intermediate



A eliminated xenon to give the perfluorinated carbene **B** which underwent rearrangement into cyclopentene **2**, Scheme 1. There are related hydrocarbon carbene intermediates in other ring contractions.^{5,6}

Alternative pathways from **1** to **2** seem to be improbable. From the literature⁷ it is known that neutral polyfluorinated 1,3- and 1,4-cyclohexadienes convert when treated with CsF in MeCN (room temperature) to thermodynamic mixtures of 1,3- and 1,4-isomers, but show no ring contraction.

[†] All experiments were carried out in polytetrafluoroethylene and FEP equipment under an argon atmosphere. (a) Sodium fluoride (0.1 mmol) was added to a solution of diene **1** (0.03–0.04 mmol) in MeCN (0.05 ml) at $-30^{\circ}C$. Xenon evolution was completed within 5–10 min at room temperature, and excess NaF was filtered off. The yield of perfluoro-3-methylenecyclopentene was 68% (^{19}F NMR). (b) A solution of SbF_5 (1.38 mmol) in SO_2FCl (0.5 ml) was added to a suspension of diene **1** (0.095 mmol) in SO_2FCl (0.2 ml) at $-50^{\circ}C$. The resulting pale-red solution was analysed by ^{19}F NMR spectroscopy. Removal of SO_2FCl at room temperature gave a viscous solution which was characterized by the same ^{19}F NMR spectrum (all resonances were broadened). Further experiments in SbF_5-SO_2 and neat SbF_5 were carried out in a similar manner.

The ionisation of polyfluorinated cyclohexadienes into polyfluorobenzenonium cations when they were treated with the strongest fluoride anion acceptor, antimony pentafluoride, is well documented.⁸ However, the ^{19}F NMR spectra of solutions of diene **1** in SbF_5-SO_2 , SbF_5-SO_2FCl or in neat SbF_5 at -50 to $+35^{\circ}C$ showed no observable carbocationic species. A freshly-prepared, pale-red solution in SbF_5-SO_2FCl displayed signals due to SbF_5 at -112 ppm, As-F at -56.6 ppm (very broad) and the cation of **1** at -89.6 (F-2), -93.2 (F-6,6), -146.2 (F-5) and -150.6 (F-4) ppm (the resonance of F-3,3 overlaps with the strong Sb-F signal) together with weak multiplets at -90 to -155 ppm which could not be assigned unambiguously. To our knowledge, diene **1** is the first example of polyfluorinated cyclohexadiene derivatives which did not give remarkable amounts of the corresponding benzenonium cation under the action of SbF_5 .

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