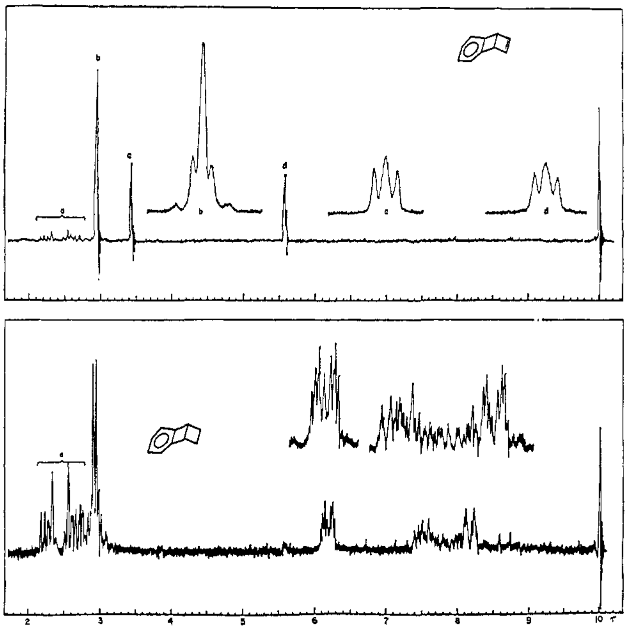

Figure 1. Nmr spectrum[4] (upper) of **1** containing 12% naphthalene (a) with the blow-ups at a sweep width of 50 cps. Nmr spectrum[4] (lower) of benzobicyclo[2.2.0]hex-2-ene (**3**, X = Y = H) containing naphthalene (a) with the blow-ups at a sweep width of 250 cps.

6.5 Hz, 4), 5.55 (bridgehead, multiplet, $J = 0.9$ Hz, 2), and 5.92 (C_5 and C_6, multiplet, $J = 0.9$ Hz, 2). The mass spectrum[5] (70 eV, direct inlet) of **4** showed the expected weak M^+ ions at m/e 198 (0.4),[6] 200 (0.25),[6] and 202 (0.1),[6] the $M^+ - Cl$ ions at m/e 163 (31.5)[6] and 165 (11.5),[6] and the $M^+ - 2Cl$ ion at m/e 128 (100).[6] Treatment of **4** with potassium *t*-butoxide in *t*-butyl alcohol afforded 2-chloronaphthalene in 69% yield.

A number of attempts to reductively dechlorinate **4** to the saturated hydrocarbon **3** (X = Y = H) failed, but did lead to mixtures of tetralin and 1,4-dihydronaphthalene. Several of these reduction products exhibited triplets in the nmr spectrum[4] at τ 3.42 and 5.58, suggesting the presence of **1**.

This was confirmed when **4** was allowed to react with disodium phenanthrene ($C_{14}H_{10}Na_2$) in dimethoxyethane. The product was isolated by trap-to-trap distillation (27% yield), and its nmr spectrum[4] (Figure 1) demonstrated that it consisted of 88% **1** and 12% naphthalene. The half-life of **1** in carbon tetrachloride was determined to be 3.96 hr at 38° (ambient probe temperature of the nmr spectrometer). The ultraviolet absorption spectrum of **1**[7] (in cyclohexane) exhibits absorptions at 257.8 (sh) (log ε 2.75), 263.4 (log ε 2.97), 270 (log ε 3.12), and 276.5 mμ (log ε 2.15) and is very similar to that reported for benzocyclobutene[8] with about a 5-mμ bathochromic shift. It therefore appears that "homoconjugation" does not exist in **1**.

Diimide reductions[9] of samples of **1** (contaminated with naphthalene and **4**) yield products containing **3** (X = Y = H). Attempted glpc separation of these components showed two major components to be present. Collection of these allowed the second component to be identified as naphthalene and the first as 1,2-dihydronaphthalene (**5**), characterized by comparison of its ultraviolet spectrum with that reported.[10] Hydrocarbon **5** undoubtedly arises by thermal ring opening of **3** (X = Y = H) to an *o*-xylylene which tautomerizes to **5**, similar to the glpc thermal rearrangement of bicyclo[2.2.0]hex-2-ene to cyclohexadiene.[11]

Separation of **3** (X = Y = H) from naphthalene can be accomplished on thin and thick layer chromatography with hexane as developer. The fastest moving material is **3** (X = Y = H) which has been characterized by its nmr spectrum[4] (Figure 1) and ultraviolet absorption spectrum (in cyclohexane) exhibiting absorptions at 262 (OD_{max} 0.94), 268 (OD_{max} 1.17), 274 (OD_{max} 1.28), and 285 mμ (OD_{max} 0.89).[12] This latter spectrum is very similar in position of absorptions and shape to those of **1** and benzocyclobutene.[8]

Acknowledgment. The authors are grateful to the National Science Foundation for their support of this research.

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(5) We thank Professor R. W. Kiser, University of Kentucky, for determination of this mass spectrum on an RMU-6E mass spectrometer.

(6) Relative abundance.

(7) The sample used contained about 5% of naphthalene (calculated from its absorption at 310 mμ), and the log ε values are *not* corrected for this impurity.

(8) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958), report the spectrum of benzocyclobutene in 95% alcohol.

(9) Catalytic reductions of "Dewar benzenes" have not proven successful with aromatization preceding reduction: R. N. McDonald and G. E. Davis, unpublished results.

(10) R. A. Freidel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951, spectrum no. 29.

(11) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).

(12) Extinction coefficients were not determined for this spectrum due to an unknown degree of contamination by naphthalene and binder from the tlc.

(13) Taken from the M.S. Thesis of D. G. Frickey.

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The Relative Fluoride Ion Donor Abilities of XeF_2, XeF_4, and XeF_6 and a Chemical Purification of XeF_4

Sir:

A number of adducts of XeF_6 with strong fluoride ion acceptors have been reported,[1-3] and the crystal structure[4] of the 1:1 adduct with platinum pentafluoride has established it as the salt $XeF_5^+[PtF_6]^-$. Recently, with others,[5,6] we have shown that xenon difluoride is also a fluoride ion donor, since the crystal structure of the 2:1 adduct with AsF_5, together with vibrational spectroscopic evidence, demonstrates that that $2XeF_2 \cdot MF_5$ adducts (M = As, Os, Ir, Pt, Ru) are the salts $Xe_2F_3^+[MF_6]^-$ and the 1:1 adducts are $XeF^+[MF_6]^-$ salts. The 1:2 adducts (M = Ir, Pt, Ru) are the salts $XeF^+[M_2F_{11}]^-$. Although it has been reported[7] that XeF_4 forms an adduct with SbF_5, this has not been properly

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(6) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *ibid.*, in press.

(7) B. Cohen and R. D. Peacock, *J. Inorg. Nucl. Chem.*, **28**, 3056 (1966).

characterized. Furthermore, XeF_4 has also been reported[8] to form XeF_2 adducts, in interaction with SbF_5 or TaF_5!

We find no evidence of adduct formation between XeF_4 and either arsenic or iridium pentafluoride, nor any indication that disporportionation to XeF_2 and XeF_6 or dissociation to $XeF_2 + F_2$ occurs. The difluoride and hexafluoride, however, each form salts with these pentafluorides. All preparations were carried out in bromine pentafluoride (bp 41.30°), with which none of the reactant fluorides forms an adduct, stable above 0°, at normal pressures. Xenon difluoride yielded, with AsF_5, the pale yellow-green salts $Xe_2F_3^+[AsF_6]^-$ (mp 99°) and $XeF^+[AsF_6]^-$ (which loses AsF_5 above 0°) and, with IrF_5, in appropriate molar proportion, $Xe_2F_3^+[IrF_6]^-$ (mp 92°), $XeF^+[IrF_6]^-$ (mp 152°) and $XeF^+[Ir_2F_{11}]^-$ (mp 69° dec). The hexafluoride gives in appropriate molar ratio with AsF_5 either $[Xe_2F_{11}]^+[AsF_6]^-$ (mp 125°) or $XeF_5^+[AsF_6]^-$ (mp 135°)[9] and with IrF_5, $[Xe_2F_{11}]^+[IrF_6]^-$ (mp 135°) or $XeF_5[IrF_6]^-$ (mp 116°). The last salt is isomorphous and almost isodimensional with $XeF_5^+[PtF_6]^-$.[4] In the XeF_4 experiments, AsF_5 and BrF_5 were removed, under vacuum, quantitatively at 0° to leave XeF_4, and, with IrF_5 as F^- acceptor, BrF_5 and XeF_4 were completely separated from the iridium fluoride under vacuum at ~20°.

Evidently XeF_6 is a better fluoride ion donor than XeF_2, since a 1:1:1 mixture with AsF_5 yielded $XeF_5^+[AsF_6]^-$. Furthermore XeF_2 does not form an adduct with PF_5 at 0°, or above, whereas $2XeF_6 \cdot PF_5$ is readily preparable.[2c]

Since XeF_4, as usually obtained, is contaminated[10] with the difluoride or hexafluoride, and the mixtures are difficult to separate physically, a chemical purification is of considerable value.

A deliberate mixture of the three binary xenon fluorides, dissolved in BrF_5, was treated with an excess of AsF_5. The BrF_5 and excess AsF_5 were vacuum distilled in a static vacuum at 0° to leave a mixture of $Xe_2F_3^+[AsF_6]^-$, $XeF_5^+[AsF_6]^-$, and XeF_4. The XeF_4 was recovered by sublimation at ~20°, in a dynamic vacuum, to a trap at −60° and was shown to be pure by its melting point, 117° (Schreiner, *et al.*, give[11] 117.1°), X-ray powder photograph, and infrared spectrum.

On the basis that the higher the effective positive charge of the xenon atom, the lower will be the possibility of fluoride ion separation, the difluoride would be anticipated to be a better fluoride ion donor than the tetrafluoride and the hexafluoride the poorest. However, XeF_6 parts with F^- more readily than XeF_2, despite the lower lattice energy for the larger cation case. Evidently the pseudo-octahedral XeF_5^+ ion ($\sim C_{4v}$ in[4] $XeF_5^+[PtF_6]^-$) is energetically especially favorable, relative to the nonoctahedral XeF_6 molecule. A similar favoring of an octahedral geometry has been demonstrated by Beaton,[12] who exploited the fluoride ion donor properties of IF_7 to effect its removal from IOF_5, by simply treating the mixture with F^- acceptor, SbF_5, to take up the former as an IF_6^+ salt. The IF_6^+ ion is octahedral[12,13] and IOF_5 nearly so.[14] A severalfold excess of IF_7 failed to displace XeF_6 from its salts; hence the potential energy of IF_6^+ relative to IF_7 is no greater than XeF_5^+ relative to XeF_6.

The relative fluoride ion donor ability, $XeF_6 > XeF_2 \gg XeF_4$, is compatible with the findings of Hyman and Quarterman, who have reported[15] that XeF_6 and XeF_2 are very soluble in anhydrous hydrogen fluoride, the former being extensively ionized, whereas XeF_4 is sparingly soluble.

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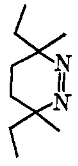
The Stereochemical Course of Cyclic Azo Decompositions

Sir:

Interest in 1,4-diradical intermediates[1] and in the photochemical and thermal decomposition of azo compounds[2-10] prompted us to investigate the stereochemical course of the decomposition of I.



I

meso- and *d,l*-I were prepared by oxidizing the corresponding *meso*- or *d,l*-3,6-diamino-3,6-dimethyloctane (II) with iodine pentafluoride at −20°.[5] A Ritter reaction[11] on 3,6-dimethyloctane-3,6-diol produced a diacetamide which was hydrolyzed to II. *meso*- and *d,l*-II could be separated by recrystallization of the diacetamide from acetonitrile. Identification of the *d,l* isomer was made by resolution of *d,l*-II *via* the hydrogen tartrate salt followed by conversion of resolved II to optically active I ($[\alpha]_{589}$ +316°, $[\alpha]_{397}$ +4200°, $[\alpha]_{350}$ −4100° (*c* 0.71, methanol)). The structure of I is supported by elemental analysis (*Anal.* Calcd: C, 71.37; H, 11.97; N, 16.65. Found: C, 71.59; H, 12.01; N, 16.53) and uv (λ_{max} 385 mμ (ϵ 145)), ir (−N=N− at 1570 cm^{-1}), and nmr spectra.

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