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 (~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 several-fold 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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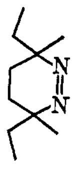
The Stereochemical Course of Cyclic Azo Decompositions

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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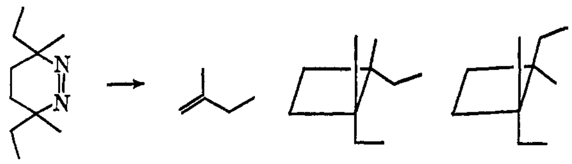
Product distributions obtained from thermolysis and direct and thioxanthone-sensitized photolyses are presented in Table I. All decompositions reported here were carried out either on 96% *meso*-I[12] containing 4% *d,l* contaminant or on 92% *d,l*-I containing 8% *meso*-I. Products were shown to be stable to the conditions of each mode of decomposition. Another product, which is as yet unidentified, was formed in less than 2% yield.

Table I. Product Distributions for Decompositions of I[a–c]

Isomer	Mode of decomposition	% III	% IV	% V	% retn of confgn in IV and V
meso	Thermal[d]	49	43	2.5	>98
d,l	Thermal[d]	51	3.5	42	>98
meso	Direct photolysis[e]	61	35	3.5	95
d,l	Direct photolysis[e]	60	4	33	97
meso	Thioxanthone sensitized[f]	77	11.5	8	61
d,l	Thioxanthone sensitized[f]	75	8	12	65

[a] Analyses by vpc on a 150-ft didecyl phthalate capillary column with toluene internal standard and by nmr with anisole internal standard agreed within 2–3%. [b] I was 0.05–0.1 M in benzene. Results were the same in cyclohexane. [c] Decompositions were carried out in thoroughly degassed, sealed tubes. [d] Samples were heated at 145–148° for 5 half-lives. [e] Incident light was of wavelength longer than 330 mμ. [f] Thiozanthone was 0.05 M and absorbed over 97% of the incident light. It is known to be an effective triplet sensitizer: W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966); W. G. Herkstroeter, A. A. Lamola, and O. S. Hammond, *ibid.*, **86**, 4537 (1964).



I III IV V

III was identified by comparison of spectra and vpc retention time with those of an authentic sample. V was identified by comparison with a sample prepared independently by hydrogenation of *trans*-1,2-divinyl-1,2-dimethylcyclobutane.[13] The structure of IV was assigned by elemental analysis and the similarity of its nmr and mass spectra to those of the *trans* isomer V. Every peak observed in the mass spectrum of IV was also observed in that of V, with small differences in the peak heights. The nmr spectrum of IV consisted of a six-proton triplet from δ 0.6 to 0.9, a six-proton singlet at δ 0.98, and an eight-proton multiplet from δ 1.2 to 1.7. That of V was essentially the same with the exception that the six-proton singlet was shifted down to δ 1.02. Decomposition of optically active I led to optically active V ([α] $-29°$), thus confirming its assignment as the *trans* isomer.

The use of benzophenone as a sensitizer led to negligible amounts of III, IV, and V but instead led to other unidentified products. Further work with this sensitizer and others is in progress.

For reasons only recently explained,[2] attempts to detect differences in the radical pairs from the singlet and triplet excited states of open-chained azo compounds have not been successful. Such differences, arising out of the greater lifetime of a radical pair having parallel rather than antiparallel electron spins, should show themselves in smaller cage effects and greater loss of configuration at the carbon atoms passing through the free-radical state from a triplet as compared to a singlet precursor. The differences recorded in Table I correspond to the expected longer lifetime of the "triplet" biradical from the cyclic azo compound I. In line with the explanation previously offered,[2] the cyclic azo triplet is unable to assume the skew conformation usual with acyclic azo compounds, and thus cannot undergo *trans–cis* isomerization, dissipate energy in internal degrees of freedom, or survive in a conformation unsuited to concerted radical-pair formation. The parallel spins in the biradical delay ring closure, allow rotation about all three single bonds separating the radical centers, and increase the cleavage to III relative to ring closure, since the eventual spin inversion which must precede reaction is now statistically likely to occur while the biradical is in a noncisoid conformation more favorable to cleavage than to ring closure.

The behavior of I presents a contrast to that of five-membered cyclic azo compounds,[7] where singlet mechanisms lead to preferred configurative inversion. The explanation offered in those cases[7] is consistent with the differences in geometry between 1,3 and 1,4 biradicals.

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The Total Synthesis of Isoiresin, Dihydroiresin, and Isodihydroiresin

Sir:

The sesquiterpene iresin (**1**)[1,2] (*Iresine celosioides*) is the first sesquiterpene in which the presence of the bicyclofarnesol skeleton typical of di- and triterpenes was demostrated. Thus, in a certain sense, iresin represents the missing link between the lower and the higher terpenes. The excellent work of Djerassi[3,4] and his collaborators led to structure **1** for iresin and to **2** and **3a** for isoiresin and dihydroiresin, respectively, also constituents of *I. celosioides*. The substantial number of asymmetric centers present in these compounds (five, four, and six, respectively), together with

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