Journal of Fluorine Chemistry, 20 (1982) 13–18

Received: April 23, 1981

RADICAL ADDITIONS OF XENON DIFLUORIDE TO CIS- AND TRANS-1-PHENYLPROPENES: COMPARISON WITH TRICHLORAMINE AND IODOBENZENE DICHLORIDE

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We would like to report data which support a free radical pathway for reaction of xenon difluoride (XeF_2) with alkenes in organic solvent. Radical intermediates have been proposed for reaction of XeF_2 to double bonds. For example, a radical pathway was suggested for the gas phase reaction of XeF_2 to ethylene and propene [1]. Zupan speculated on a radical cation pathway for the acid catalyzed reaction of XeF_2 with alkenes but gave no experimental evidence for this mechanism [2,3]. Radical cation intermediates were demonstrated for the reaction of XeF_2 to aromatics by Filler [4]. Acid catalyzed ionic reactions to unsaturated hydrocarbons have been reviewed [5].

Zupan and Pollak have shown that alkenes do not react in aprotic solvent with XeF_2 at low concentrations of alkene unless acid catalyst is present [3]. However, we observed that illumination of a dilute solution of cis- or trans-1-phenylpropenes (I) or (II) in methylene chloride at 0° with a 270 watt sunlamp produced IIIa and IIIb in less then two hours (Table). Furthermore, at high concentration of (I) and (II), a spontaneous reaction occurred in the dark between XeF_2 and these styrenes. The reaction conditions for both of these reactions imply a radical mechanism - the latter a molecule-induced pathway.

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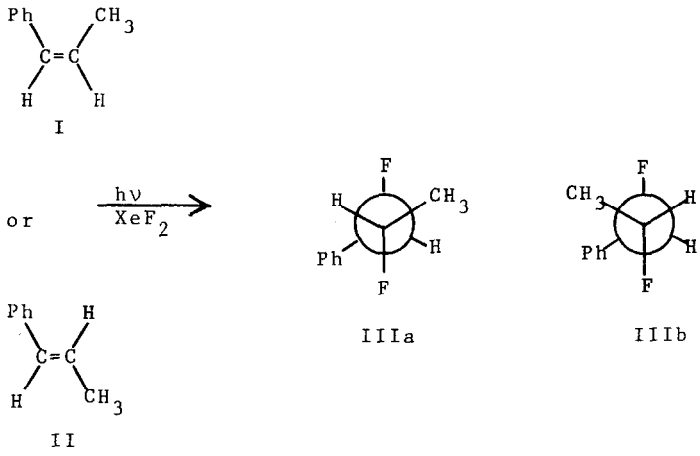


It is conceivable that these reactions are catalyzed by a trace of HF produced from hydrogen abstraction or from trace impurity in the XeF_2. To eliminate a possible ionic pathway, we repeated the photochemical and dark reactions in the presence of two equivalents of pyridine [6]. Our assumption was that the pyridine would remove any trace of HF. The results did not differ from those without pyridine as shown in the table. Therefore, we conclude that reactions of XeF_2 with (I) or (II) under these conditions must proceed by a free radical pathway since the reactions are not acid catalyzed, and the dilute reactions do not proceed without illumination. Unfortunately this radical reaction with XeF_2 does not appear to represent a general synthesis since reaction with alkenes such as 1-hexene, cyclohexene, and 2,3-dimethyl-2-butene does not give vicinal difluoride products. The major component of these reactions are unreacted alkene and minor amounts of low boiling products - presumably fluorine substitution along the alkyl chain.

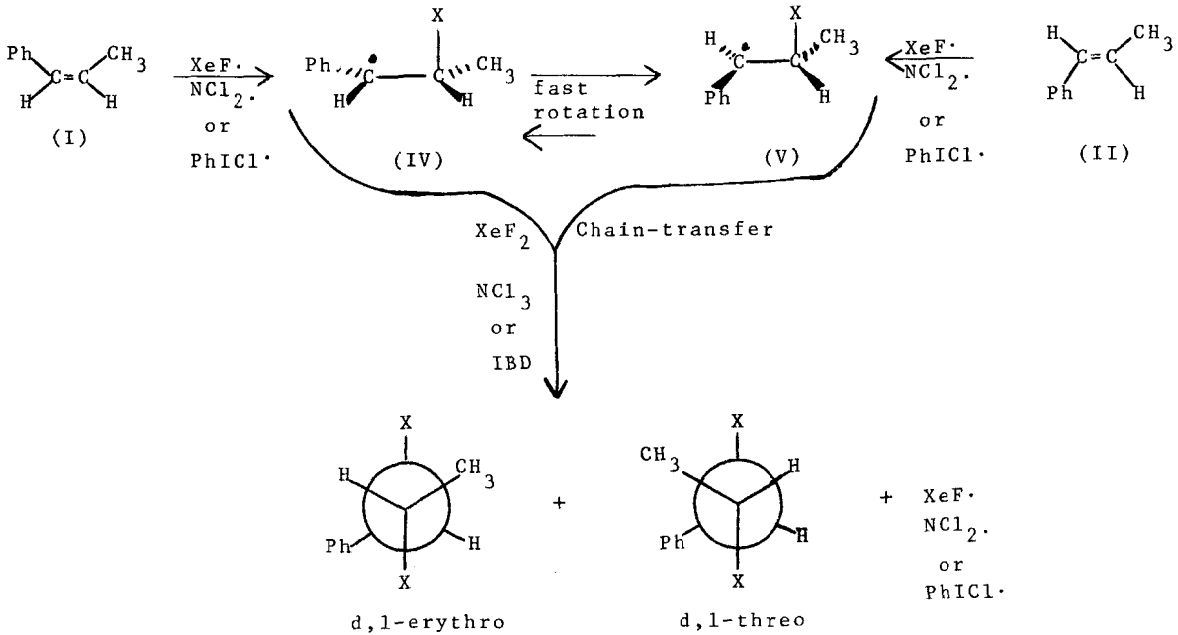
TABLE

Radical Reactions of Halogen Systems to Styrenes (I) and (II)

Halogen Systems (conditions)	Mole Fraction Styrene in CH_2Cl_2	Percent Products[a] From cis-1-phenylpropene		From trans-1-phenylpropene	
		erythro	threo	erythro	threo
XeF_2[b] (hν)	0.10[c]	58	42	56	44
XeF_2[d] (dark)	0.50	59	41	52	48
NCl_3[b] (hν)	0.02	77	23	76	24
IBD[d] (hν)	0.02	91	9	92	8

[a]Reaction (percent yield); XeF_2 (60-75); NCl_3 (87-88); IBD (100). [b]Reaction temperature 0°. [c]Similar results were observed at 0.02 mole fraction alkene. Molecule-induced reactions can occur above 0.10 mole fraction alkene. [d]Reaction temperature at 25°.

For comparison, we treated (I) and (II) with iodobenzene dichloride (IBD) and trichloramine (NCl_3). These chlorinating agents are known to react via a radical pathway [7,8]. The data show that reaction of (I) and (II) with IBD, NCl_3, and XeF_2 under radical conditions are stereoselective in that the erythro products are preferred (Table). The erythro products (IIIa, VIa) probably predominate because anti-rather than syn-attack on intermediate (V) is the preferred pathway (Scheme). An increase in steroselectivity from XeF_2, NCl_3 to IBD is expected for these radical reactions because steric interactions in the chain-transfer step are greatest for IBD and less important for the smaller and linear XeF_2 molecule. A similar steric effect has been reported for the radical reaction of IBD with cyclic alkenes [7,9].



XeF_2 (X = F)	(IIIa)	(IIIb)
IBD or NCl_3 (X = Cl)	(VIa)	(VIb)

SCHEME. Propagation and Chain - Transfer Steps

EXPERIMENTAL

To a solution of olefin (I) or (II), dissolved in methylene chloride to give the mole fractions shown in the Table, was added 1.0 m mole halogenating reagent at 0 or 25° (Table) in such amounts to consume 30 percent of the olefin. Addition of XeF_2 and IBD were as solids while NCl_3 was added as a 1.0 M solution in methylene chloride. Chlorinations were conducted under nitrogen as described in the literature because radical chlorinations are inhibited by oxygen [7,8,9] . Fluorination with XeF_2 can be performed without inert atmosphere since this radical reaction is not inhibited by oxygen [10] . Illumination was from a 270 watt sunlamp.

Difluorides (IIIa) and (IIIb) were isolated by preparative vpc and identified by comparing their nmr spectra with those reported previously [11] . Vpc analysis conditions: 14' x ¼" column (SS) at 120° packed with FFAP (2.5%) on 80-100 mesh Chromosorb W with retention times (min) of 15.0 (IIIa) and 17.3 (IIIb). The dichlorides (VIa) and (VIb) were isolated by preparative vpc and identified by comparing their spectra with those reported previously [12] . Vpc analysis conditions: 6' x ¼" column (SS) at 65° packed with SE-30 (2.5%) on 60-80 mesh Chromosorb W with retention times (min) of 28.7 (VIa) and 32.4 (VIb). Control experiments with (IIIa), (IIIb), (VIa), and (VIb) show that they are stable to reaction and analysis conditions.

ACKNOWLEDGEMENT

This work was supported by the Research Corporation, the Research Associates of Point Loma College, and the Catalysts of Bethany Nazarene College.

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