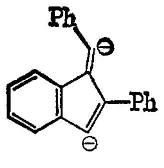
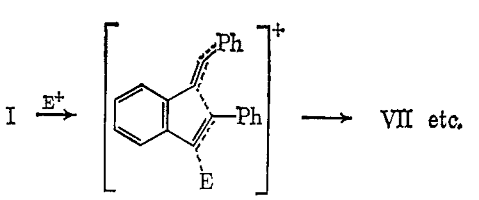
The domino folding of the triple bonds in I is not limited to attack of electrophiles. Irradiation of I and thiophenol gave an unstable yellow 1:1 adduct identified spectrally as a benzofulvene. Reaction of I with lithium or lithium naphthalenide in tetrahydrofuran gave after protonation fulvene VIa.[9] Addition of deuterium oxide to the reaction mixture afforded doubly deuterated VIa, but whether or not the fulvene dianion VIII is the kinetic or thermodynamic product of this metallation is presently unclear. Reduction in the presence of proton donors (lithium in methanol and ammonia) led only to the uncyclized products *o*-bis(2-phenylethyl)benzene and *o*-styrylbibenzyl.[10]

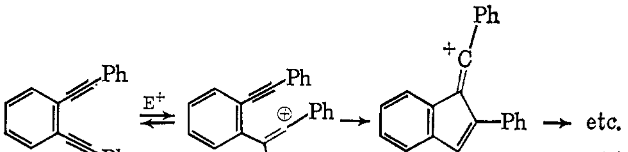


VIII

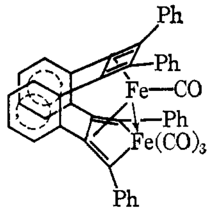
We tentatively suggest that the behavior of I toward electrophiles represents a concerted ring closure *via* the transition state represented in eq 1. The main evidence for this lies in the observed rate enhancement of electrophilic attack on I compared to tolane which, considering the inductively deactivating effect of the neighboring acetylene,[11] is substantial. If one abandons the restrictions imposed by a rate-determining irreversible initial attack of the electrophile,[8,12] however, an equally plausible mechanism involving intramolecular siphoning off of a reversibly formed intermediate as in eq 2 can be formulated. We cannot presently decide between these.



(1)



(2)



IX

Probably the most interesting feature of the above reactions is their contrast with the behavior of I on irradiation[1] and on reaction with iron pentacarbonyl. The latter affords several related dimeric complexes, one of which possesses[13] structure IX, while the former affords a product apparently derived from a closely related carbon skeleton. The difference in the two sets of reaction probably results from: (1) in the absence of capturing agents, domino folding can only lead to polymerization, and (2) the yields of the dimeric products are relatively low.

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[9] As expected, according to the investigation of D. Y. Curtin and W. J. Koehl, *J. Am. Chem. Soc.*, **84** (1967) (1962).

[10] S. A. Kandil and R. E. Dessy, *ibid.*, **88**, 3027 (1966), have recently reported similar examples of intramolecular anionic attack on acetylenes.

[11] P. E. Peterson and R. J. Kamat, *ibid.*, **88**, 3152 (1966).

[12] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.*, 394 (1965).

[13] L. F. Dahl, personal communication.

[14] A. P. Sloan Fellow.

The Kinetics of the Basic Hydrolysis of Difluoramine

Sir:

Difluoramine has been found to undergo basic hydrolysis in aqueous solution to yield difluorodiazine (N_2F_2).[1,2] Early speculations on the mechanism of this reaction suggested that ionization of HNF_2 to yield H^+ and NF_2^- was involved. We have analyzed the products of the reactions of difluoramine with a variety of anions and have found HNF_2 is quite susceptible to anionic attack in general.

The reaction of difluoramine with excess hydroxyl ion in water yields approximately 60% N_2F_2 and 20% nitrogen. The remainder of the nitrogen-containing products are varying amounts of N_2F_4, N_2O, NO_3^-, and NO_2^-. Preliminary experiments with a variety of anions gave rate data which indicate that the reaction is generally base catalyzed (see Table I). The kinetics of the reactions with these anions are currently being studied in greater detail. In this communication we report the detailed results with hydroxyl ion.

Table I. Approximate Rate Constants for the Attack of Anions on HNF_2

Anion	K_2, M^{-1} sec^{-1}
CN^-	4.6×10^{-2}
NCS^-	1.8×10^{-2}
Br^-	$\sim 8 \times 10^{-3}$
$H_2PO_4^-$	5.8×10^{-3}
Cl^-	$\sim 5 \times 10^{-4}$
OAc^-	4.7×10^{-5}

The reaction of HNF_2 was studied over the range of pH 7 to 9.3. The concentration of HNF_2 in solution was measured accurately as a function of time by means of the polarographic reduction of HNF_2.[3]

Polarograms were recorded with a Sargent Model XXI polarograph. A standard H cell and saturated calomel reference electrode were used, and the polaro-

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[1] G. A. Ward and C. M. Wright, *J. Am. Chem. Soc.*, **86**, 4333 (1964).

[2] K. J. Martin, *ibid.*, **87**, 394 (1965).

[3] G. A. Ward, C. M. Wright, and A. D. Craig, *ibid.*, **88**, 713 (1966).

graphic solution was maintained at constant temperature by immersing the cell in a constant-temperature water bath. A small combination electrode (Sargent S-30070-10) placed in the sample compartment of the H cell and a Beckman Zeromatic pH meter were used to monitor the sample pH during kinetic runs. More accurate pH measurements were made before and after each run with a Beckman Model 1019 research pH meter, a Beckman 41263 pH electrode, and a Sargent S-30080-15C reference electrode.

Difluoramine was prepared by hydrolysis of trityldifluoramine,[4] and 0.1 *M* stock solutions were prepared by dissolving sufficient HNF_2 in deaerated water. These stock solutions were stored in glass under nitrogen.

For reactions with a half-life of 30 min or less, the following procedure was used. Fifteen milliliters of buffer solution, containing 7% methanol by volume, was placed in the sample compartment of the H cell, deaerated with N_2, and allowed to reach a constant (25°) temperature. The potential of the dropping mercury electrode (dme) was set at -1.5 v *vs.* saturated calomel electrode (sce), and the current was recorded as a function of time. After the residual current was recorded for approximately 1 min, 0.08 to 0.75 ml of HNF_2 stock solution was injected into the buffer by means of a hypodermic syringe. The solution was then mixed for 15 sec with a magnetic stirrer in the H cell. After the solution was allowed to come to rest for approximately 1–2 min, the diffusion current was measured continuously as a function of time, at -1.5 v. The residual current was monitored by periodically setting the applied voltage to -0.8 v and measuring the current at that point.

For slower reactions, the reaction was carried out in a capped glass bottle. The concentration of HNF_2 in these reactions was monitored by periodically withdrawing an aliquot of the solution and analyzing it polarographically in a pH 7 buffer solution.

A table of the polarographic diffusion current as a function of reaction time was prepared from the polarographic data for each kinetic run. From these data the first-order least-squares rate constant of the reaction was calculated with a Fortran computer program. This program calculates a rate constant (k) and an effective concentration C_0 at time $t = 0$ in the least-squares sense; that is, k and C_0 are such that

$$F(k, C_0) = \sum_{i=1}^{n} (\ln C_i - \ln C_0 + kt_i)^2$$

is a minimum. C_i and t_i are the experimental concentration and time data points in this expression.

The data from 47 kinetic runs (about eight points were taken per run) were analyzed with the program described above and the results are given in Table II.

Table II. Rate Constants for the Attack of OH^- on HNF_2

pH	K_1, sec^{-1}	K_2, M^{-1} sec^{-1}
7.03	0.170×10^{-3}	15.88×10^{2}
7.83	0.517×10^{-3}	7.65×10^{2}
8.14	0.950×10^{-3}	7.04×10^{2}
8.35	1.47×10^{-3}	6.59×10^{2}
8.70	3.71×10^{-3}	7.41×10^{2}
8.95	5.89×10^{-3}	6.62×10^{2}
9.24	12.02×10^{-3}	6.91×10^{2}

Good first-order plots of the log of HNF_2 concentration *vs.* time were obtained at each pH level.

The pH 7.03 and 7.83 buffers were NaH_2PO_4–Na_2HPO_4 systems, the pH 8.14 through 8.95 buffers were borate, and the pH 9.24 buffer was 0.1 *M* NH_4Cl–0.1 *M* NH_4OH. K_2 is calculated from the relationship

$$K_1 = K_2[OH^-]$$

The values of K_2 at pH 7.03 and 7.83 are high, probably because of contributions from the anions of the buffer, *i.e.*, $H_2PO_4^-$ and HPO_4^{2-} which were found to attack HNF_2 in aqueous solution. The average of the remaining K_2 values is 6.92×10^2 M^{-1} sec^{-1}.

Methanol was added to all the reaction solutions to prevent the formation of N_2F_2, which gives a polarographic wave at a less cathodic potential than HNF_2 and interferes with the measurement of HNF_2 concentration by polarography. We have found that the addition of methanol or any type of C–H material to aqueous systems with pH values greater than 7 causes essentially all of the difluoramine nitrogen which undergoes reaction to end up as nitrogen gas. The rationale offered for this observation is that a reactive intermediate species such as NF abstracts hydrogen from the C–H substrate and then goes to nitrogen *via* coupling and subsequent dehydrofluorination reactions.

The effect of methanol concentration on the rate of reaction was studied by varying the CH_3OH content of the solution from 3 to 20% at pH 8.97 and by determining the rate of the reaction in the absence of methanol at three different pH values. There was no trend in the data obtained at pH 8.97, and K_1 averaged 5.62×10^{-3} sec^{-1}. The values of K_1 obtained in the absence of methanol at pH values of 8.97, 8.70, and 8.35 were 5.63×10^{-3}, 3.92×10^{-3}, and 1.56×10^{-3} sec^{-1}, respectively. These values are very close to the corresponding values of K_1 given in Table II. These data indicate that methanol has no effect on the rate-determining step of the reaction.

The effect of buffer concentration on the rate of the reaction was studied over the range 0.1 to 0.01 *M*. No change in rate was observed for any of the buffers unless the buffer capacity was exceeded. The HNF_2 concentration was similarly varied from 5.3×10^{-4} to 5.0×10^{-3} *M*. No effect on rate could be noted. The attack of borate anion on HNF_2 apparently has little contribution to the decomposition of HNF_2 in basic solution. A preliminary value for the second-order rate constant for Cl^- was found to be 5.1×10^{-4} M^{-1} sec^{-1}. Thus, there is a slight effect of chloride ion on the K_2 obtained in the pH 9.24 NH_4Cl-NH_4OH buffer. Fluoride ion was found to attack HNF_2 at a rate which was barely detectable. Thus, the fluoride ion generated in the hydrolysis reaction has little if any effect on the rate-determining step of the reaction.

We feel that the kinetic data obtained for the basic hydrolysis show that the attack of OH^- on HNF_2 is a second-order reaction and that there is little or no contribution from an ionization of HNF_2. Nitrogen trifluoride has been reported to undergo nucleophilic attack by hydroxyl ion *via* an SN2 mechanism.[5] The attack of base on HNF_2, however, may be *via* either an SN2 mechanism or *via* an assisted SN1 mechanism.

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(4) W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963).

(5) G. L. Hurst and S. I. Khayat in "Advanced Propellant Chemistry," R. F. Gould, Ed., Advances in Chemistry Series, No. 54, American Chemical Society, Washington, D. C., 1966, p 245 ff.

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The Direct Chlorination of Pentaborane(9)

Sir:

The previously unreported 1-chloropentaborane(9)[1] can be prepared in greater than 90% yields by the direct chlorination of pentaborane in the presence of aluminum chloride. In the absence of this catalyst 2-chloropentaborane[2] is by far the most predominant isomer, but so far the yields have not exceeded 30%.

In a typical experiment 6.5 mmoles of chlorine, 11.6 mmoles of pentaborane, about 1 g of aluminum chloride, and 13 ml of boron trichloride were condensed into a reaction flask on the vacuum line.[3] The flask was then sealed from the vacuum line and warmed from −108 to 0° over a 2-hr period and maintained at 0° for 18 hr. Separation of the reaction mixture by fractional condensation resulted in the isolation of 6.0 mmoles (92% based on chlorine) of 1-chloropentaborane. The mass spectrum of 1-chloropentaborane is almost identical with that of 2-chloropentaborane (some relative intensities are different). The ^{11}B nmr spectrum (32.1 Mc) is similar to that of other 1-halopentaboranes, consisting of a doublet at $\delta = 11.9$ ppm ($BF_3 \cdot O(C_2H_5)_2 = 0.0$), $J = 170 \pm 5$ cps, corresponding to B^{2-5}–H, and a singlet at $\delta = 29.3$ ppm corresponding to B^1–Cl with an area ratio of 4.0:1.0, respectively. The ^{1}H nmr spectrum (100 Mc) consists of a quartet of equally intense lines at τ 7.07, $J = 165 \pm 5$ cps, corresponding to the four identical terminal hydrogens bonded to ^{11}B, and a broad resonance at τ 11.27, corresponding to an equal number (area ratio 1.00 ± 0.03) of bridging hydrogens. The melting range of 1-chloropentaborane is 26–27° and its vapor pressure at 28° is 4.2 mm. The gas-phase infrared spectrum contains bands at: 2610 (s), 1840 (w), 1785 (w), 1610 (vw), 1435 (m), 1380 (m), 1200 (m), 1160 (m), 1065 (w), 905 (m), 855 (w), 765 (w), and 635 (m) cm^{-1}.

A similar reaction was attempted in the absence of aluminum chloride. In this case only traces of 1-chloropentaborane were observed, but a 15% yield of 2-chloropentaborane (based on chlorine) was obtained. Low-temperature liquid-phase reactions and low-pressure gas-phase reactions were carried out in an attempt to improve the yield of 2-chloropentaborane, but in all cases the yields have been between 10 and 30%.

A previous attempt to chlorinate pentaborane in the presence of aluminum chloride in carbon disulfide solution was reported[4] to yield "microquantities" of a chloropentaborane contaminated with carbon tetrachloride, and attempts to duplicate the reaction on a larger scale resulted in explosions.[5]

It appears that in the absence of a strong Lewis acid the chlorination of pentaborane is a radical reaction. By contrast, halogenations with bromine and iodine produce 1-halopentaboranes almost exclusively and in high yields. These reactions can be envisioned as occurring *via* heterolytic cleavage of the halogen followed by electrophilic displacement of a proton from the 1 position in pentaborane by the positive halogen. This is similar in concept to the chlorination in the presence of aluminum chloride, a strong heterolytic catalyst.

The assumption that the uncatalyzed chlorination of pentaborane is a radical reaction is supported by the following observations. First, when the bromination of pentaborane is carried out in the presence of strong ultraviolet irradiation, the reaction proceeds about 100 times faster than usual,[6] and the ratio of 2-bromo- to 1-bromopentaborane increases from the value 0.049 reported by Burg and Sandhu[7] to 1.2 (although the total yield of bromopentaboranes decreases to about 45%, based on bromine). Second, attempts to chlorinate pentaborane with ICl and ICl_3 resulted in the formation of 1-iodopentaborane, in both cases in greater than 90% yields. Further studies of the halogenation of pentaborane are in progress and will be reported shortly.

Acknowledgment. We wish to thank the National Science Foundation and the Wisconsin Alumni Research Foundation for support of this research.

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[1] All pentaboranes referred to in this communication are derivatives of pentaborane(9), B_5H_9.

[2] T. Onak and G. B. Dunks, *Inorg. Chem.*, 3, 1060 (1964).

[3] R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[4] I. Shapiro and H. Landesman, *J. Chem. Phys.*, 33, 1590 (1960).

[5] Pentaborane forms shock-sensitive mixtures with carbon tetrachloride: "Pentaborane," Callery Chemical Co. Technical Bulletin CT-1300, Oct 1, 1961, and references therein.

[6] L. H. Hall, V. V. Subbanna, and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 3969 (1964).

[7] A. B. Burg and J. S. Sandhu, *ibid.*, **87**, 3787 (1965).

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$S = 1$ Ground State in Six-Coordinated Iron(II)

Sir:

We wish to report here on some results which demonstrate that $S = 1$ ground states may be stabilized in *six-coordinated* d^6 complex compounds. So far, triplet ground states have been assumed in d^6 configuration for square-planar iron(II) systems only, and even there not more than two examples were found.[1,2]

In what follows, the compounds $[Fe(phen)_2ox] \cdot 5H_2O$ (I) and $[Fe(phen)_2mal] \cdot 7H_2O$ (II), where phen = 1,10-phenanthroline, ox = oxalate, and mal = malonate, will be used as examples. Analogous results were obtained for the corresponding compounds where phenanthroline has been replaced by 4,7-dimethyl-1,10-phenanthroline or 2,2′-bipyridyl[3] as well as for $[Fe(phen)_2F_2] \cdot 4H_2O$.

Magnetic susceptibilities were measured repeatedly in an atmosphere of 400 μ pressure of nitrogen on 20- to

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[1] A. B. P. Lever, *J. Chem. Soc.*, 1821 (1965).

[2] J. Chatt and B. L. Shaw, *ibid.*, 285 (1961).

[3] The formulas of these compounds differ from those of the phenanthroline series in the amount of water of crystallization.