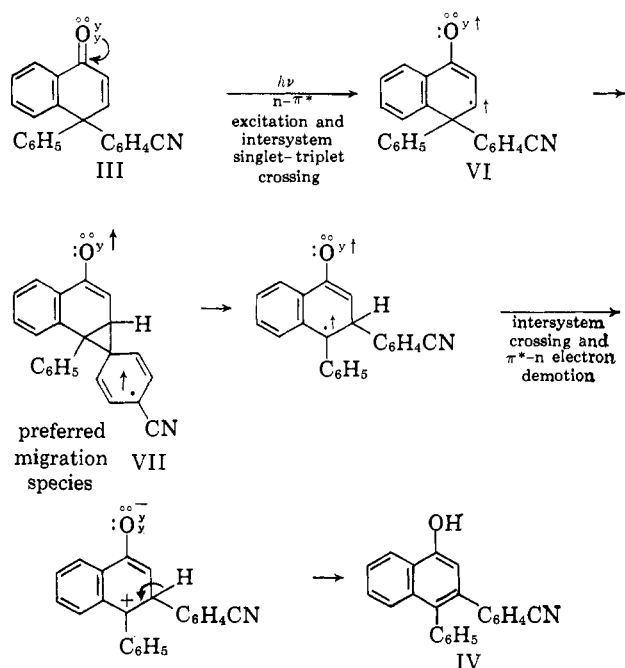


The preferential migration of *p*-cyanophenyl over phenyl in the rearrangement of the triplet excited state of III, contrasted with the dark acid-catalyzed rearrangement (giving only V), clearly indicates that the β -carbon atom (*i.e.*, C-3) does not exhibit electron-deficient reactivity. This suggests that $^+C-C=C-O^-$ is a poor representation of the excited state and that the migrating aryl group does not become electron deficient prior to the product-limiting stage of the rearrangement. Preferred phenyl over methyl migration rules out the possibility that more stabilization is derived from the nonmigrating group. The observed results do not give evidence whether the β -carbon is odd electron in capability, electron rich, or both. The results are consistent with a picture involving reaction of the $n-\pi^*$ triplet VI as depicted in Chart I. Available evidence suggests that the lowest energy triplet is indeed $n-\pi^*$. We plan to report in the future on migratory behavior of other groups and on evidence dealing with the electron distribution in the triplet prior to reaction.



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The Reaction of Antimony(V) Fluoride with Tetrafluorohydrazine

Sir:

The recent study on the Lewis basicity of difluoramine and alkyldifluoramines¹ prompts us to report the

(1) A. D. Craig, *Inorg. Chem.*, **3**, 1628 (1964).

isolation of a new type of complex in which tetrafluorohydrazine apparently behaves as a base (or possibly as a fluoride donor). Treatment of $AsF_3SbF_5^2$ in arsenic(III) fluoride solution with excess tetrafluorohydrazine³ at partial pressures greater than 400 mm. produced a solid complex having the empirical formula NF_2SbF_5 , m.p. 118–120° (*Anal. Calcd.*: N, 5.20; Sb, 45.4. Found: N, 5.26; Sb, 45.1). If tetrafluorohydrazine, even though in excess, was allowed to react at partial pressures below 100 mm., another material whose composition approached $(NF_2)_2(SbF_5)_3$, m.p. 72–74° (*Anal. Calcd.*: N, 3.71; Sb, 48.5. Found: N, 3.56; Sb, 48.1), was obtained. The latter complex could be converted to NF_2SbF_5 by either further treatment with tetrafluorohydrazine at a partial pressure of 400 mm. or by extraction with sulfur dioxide at –45°. Although arsenic(III) fluoride and sulfur dioxide are suitable solvents for NF_2SbF_5 at lower temperatures, they react with NF_2SbF_5 slowly at ambient temperature.

The complex NF_2SbF_5 was apparently stable and nonvolatile at temperatures up to its melting point, and its thermal dissociation into tetrafluorohydrazine and antimony(V) fluoride was not complete in 15 min. at 150°. At 200°, however, a semiquantitative recovery of tetrafluorohydrazine was achieved. Similarly, displacement of the tetrafluorohydrazine from the complex by fluoride ion occurred in 98% yield when it was heated to 125° in the presence of a large excess of dry potassium fluoride.

The infrared spectrum of NF_2SbF_5 was obtained on numerous samples using antimony(V) fluoride as a mulling agent or on powders with no mulling agent present.⁴ The two sets of spectra were identical except for small differences in the SbF region. The principal bands of the spectrum occurred at 1300 (ms), 1124 (ms), 926 (ms), 666 (vs), and 498 cm^{-1} (m). The two bands at 926 and 1124 cm^{-1} are attributed to NF stretching modes.⁵ The broad band at 666 cm^{-1} is in the $Sb-F$ stretching region⁶ and greatly resembles in shape and relative intensity the strong, broad band observed at 674 cm^{-1} in the spectrum of sodium hexafluoroantimonate. The presence of a hexafluoroantimonate ion in the complex is thus possible. The origin of the band at 1300 cm^{-1} is not known but could also be due to the NF moiety. The shift to higher frequencies of the bands attributed to the N-F stretching modes is in agreement with either a molecular or an ionic structure for the complex. The e.p.r. spectrum of NF_2SbF_5 showed no evidence for the presence of an unpaired electron under three conditions: the solid state, in a solution of SO_2 at –70°, or in AsF_3 solution at –5°. Thus it is concluded either that the N-N bond in N_2F_4 is intact, or that the complex has undergone heterolytic cleavage. The F^{19} n.m.r. spectrum of NF_2SbF_5 was obtained in SO_2 solution at –70°. It was complex and, unfortunately, it was not possible to obtain a sufficiently concentrated solution so that a reliable determination of the relative peak areas could be made.

(2) A. A. Woolf and N. N. Greenwood, *J. Chem. Soc.*, 2200 (1950).

(3) Caution should be exercised in handling N_2F_4 and N_2F_2 especially in the presence of organic materials.

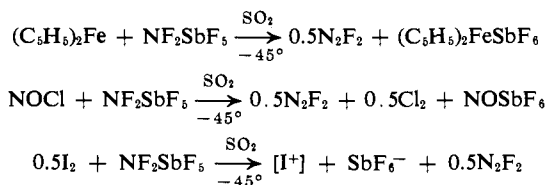
(4) Silver chloride plates were employed since NF_2SbF_5 was found to react with sodium chloride.

(5) J. R. Durig and R. C. Lord, *Spectrochim. Acta*, **19**, 1877 (1963).

(6) L. K. Akers, Ph.D. Thesis, Vanderbilt University, 1955.

In the spectrum there appear to be three types of NF fluorines; two of these are coupled to form an AB or A₂B₂ group which is centered at -144 ϕ , and the third which is at -192 ϕ is apparently uncoupled. Two bands were observed in the SbF⁷ region at 134 and 114 ϕ . A search for a more suitable media for obtaining the n.m.r. spectrum is underway.

Reaction of NF₂SbF₅ with species capable of being oxidized produced *trans*-N₂F₂ in about 90% yield. Several such reactions are



These reactions could also be carried out in arsenic(III) fluoride at -6 to -8° with similar yields. Characterization of the antimony species was performed in the first two cases only.

Acknowledgment. This work was performed under Army Ordnance Contract No. DA-01-021 ORD-11878.

(7) C. H. Hoffmann, B. E. Holder, and W. L. Jolly, *J. Phys. Chem.*, **62**, 364 (1958).

John K. Ruff

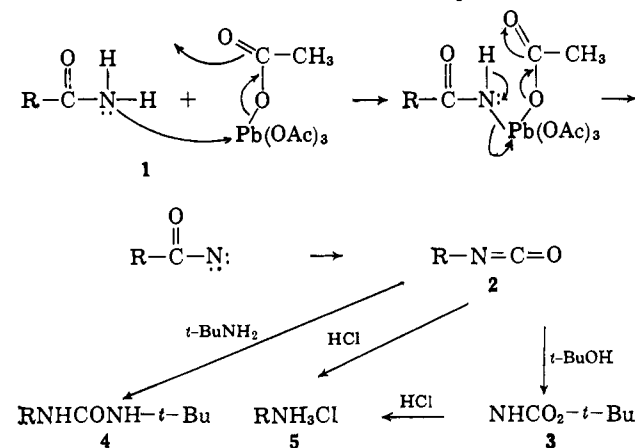
Rohm & Haas Company, Redstone Arsenal Research Division
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Received December 21, 1964

Reactions of Amines. XIV. An Oxidative Rearrangement of Amides^{1,2}

Sir:

In an earlier communication³ we reported an oxidative rearrangement of the N-amino amide, 1-amino-oxindole, to 3-cinnolinol, a reaction presumably pro-



ceeding through a nitrene intermediate. More recently Campbell and Rees⁴ have described the preparation of benzyne from 1-aminobenzotriazole *via* an oxidative elimination that also appears to proceed through a nitrene intermediate. In both of these reactions the oxidizing agent was lead tetraacetate.

(1) Paper XIII: *J. Org. Chem.*, in press.

(2) This work was supported in part by Public Health Service Research Grant CA-3090 from the National Cancer Institute.

(3) H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Am. Chem. Soc.*, **82**, 3977 (1960).

(4) C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 296 (1964).

We now report an oxidative rearrangement of simple amides using lead tetraacetate that yields products similar to those obtained from the Hofmann rearrangement.⁵ Thus, under suitable reaction conditions⁶ a number of aliphatic and aromatic amides could be quickly converted into the corresponding isocyanates **2** or their derivatives (3-5) in moderate to excellent yields. The mechanism shown is a greatly simplified one, reasonably consistent with the present understanding of lead tetraacetate oxidations⁷ and our observations on this new reaction.

Simple aliphatic amides did not react appreciably with lead tetraacetate in acetic acid and reacted only sluggishly in nonpolar solvents such as benzene, chloroform, or methylene chloride. They reacted moderately rapidly in *t*-butyl alcohol and quite rapidly in this solvent in the presence of added triethylamine or, preferably, in dimethylformamide (without added base). These observations can be rationalized in part in terms of solvation effects and in part in terms of base catalysis, the base probably assisting in the removal of the proton in the second stage of the reaction. Aromatic amides were less reactive and reacted most satisfactorily in dimethylformamide with added triethylamine.

These reaction conditions were sufficiently vigorous to preclude the use of amides with functional groups capable of reacting with lead tetraacetate under milder conditions, *e.g.*, active methylene groups (phenylacetamide) and olefinic double bonds (cinnamamide).

When the reaction was run in *t*-butyl alcohol, the product isolated was the *t*-butylurethan **3**. The use of triethylamine in these reactions appeared to accelerate not only the oxidative rearrangement but also the reaction of the isocyanate with the alcohol, minimizing thereby the dehydration of the latter. Typical yields were; *t*-butyl-*N*-cyclohexylcarbamate,⁸ m.p. 78-78.5°, 30% from cyclohexanecarboxamide; *t*-butyl-*N*-cyclobutylcarbamate,⁸ m.p. 81°, 62% from cyclobutanecarboxamide; *t*-butyl carbanilate, m.p. 133-136° (lit.⁹ m.p. 135-136°), 76% from benzamide; *t*-butyl *p*-chlorocarbanilate,⁸ m.p. 105-106°, 71% from *p*-chlorobenzamide.

Methyl and ethyl alcohols could not be substituted for *t*-butyl alcohol for these alcohols reacted more rapidly with the reagent than did the amides.

Cleavage of the *t*-butylurethans with hydrogen chloride in ether proceeded rapidly to give high yields of the amine hydrochlorides **5**, *e.g.*, cyclohexylamine hydrochloride, 96%, cyclobutylamine hydrochloride, 79%, *p*-chloroaniline hydrochloride, 83%.

When the reaction was run in dimethylformamide, the isocyanate **2** could be isolated but isolation in most of the examples in this work was complicated by similarities in boiling point between product and solvent. For example, from the oxidative rearrangement of pivalamide a 44% yield of pure *t*-butyl isocyanate

(5) P. A. S. Smith, "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1964.

(6) Amides, being less basic than N-amino amides, require more strenuous reaction conditions than N-amino amides.

(7) R. Criegee, "Newer Methods of Preparative Organic Chemistry," Vol. I, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1948, p. 16; Vol. II, p. 368, 1963.

(8) All products gave elemental analyses and infrared spectra compatible with assigned structures. Where solubility permitted, additional confirmation was obtained from n.m.r. spectra.

(9) E. Knoevenagel, *Ann.*, **343**, 46 (1905).