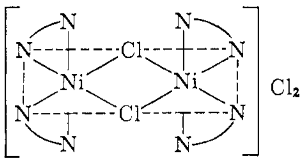
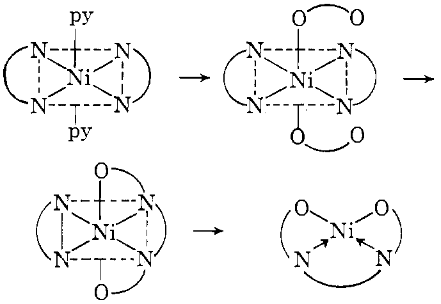


B

in the destruction of B. However, in view of the recent report[2] that B is actually a dimer with bridging chloride ions, it seems likely that treatment of B with pyridine would result in the formation of *trans*-$[Ni(en)_2(py)_2]^{2+}$. An oxygen atom from each of two β-diketone molecules then could replace a molecule of pyridine and condense with an adjacent coördinated amino group.



This scheme may not represent the exact sequence of reaction steps, but it shows the template mechanism. It is supported by the observation that β-diketones do not condense with $[Ni(en)_3]Cl_2$.

It is worth noting that only catalytic amounts of pyridine are required and that the desired condensation does not occur if the base is added after B and the β-diketone are mixed. This is probably an indication that a labile proton from the β-diketone is combining with the base to nullify its catalytic properties. Moreover, no reaction is observed when aqueous solutions of B and sodium acetylacetonate are mixed. This suggests that the condensation does not involve direct removal of bridging chloride ions by a β-diketone or its conjugate base.

The preparation of compounds of type A_1, A_2 (Table I) is exemplified by the condensation of acetylacetone and B. To a solution of B (2.49 g. or 0.005 mole in 20 ml. of water) was added two drops of pyridine followed by acetylacetone (1.98 g., 0.02 mole). The mixture was allowed to reflux for 2 hr., during which time the product crystallized in quantitative yield. Even though some of the β-diketones studied do not dissolve in water, they readily take part in the condensation.

Condensation of acetylacetone also was noted when butylamine or 2,4-lutidine was used as catalyst; 2,6-lutidine gave no reaction. The latter failure can be attributed to the steric hindrance of the two methyl groups on the base and would seem to indicate that replacement of the bridge chlorine atoms by a coördinating base is necessary for condensation to occur.

Further investigation of the scope, kinetics, and mehanism of the reaction is in progress.

TABLE I

PROPERTIES OF COMPOUNDS OF THE TYPE A_1 AND A_2 PREPARED BY PYRIDINE-CATALYZED CONDENSATION OF β-DIKETONES AND RELATED COMPOUNDS WITH B

Ligands	M.p., °C.	Yield, %	Analysis[a] C	H	N	Ref.
Acetylacetone	198	82	51.25[b]	6.4	9.97	[c]
			51.75	6.44	9.69	
Benzoylacetone	290	86	65.23	5.44	6.92	[d]
			64.53	5.44	6.96	
o-Hydroxy-acetophenone	290	81	61.24	5.10	7.94	
			61.72	5.47	8.27	
Salicylaldehyde	350	94	58.83	4.31	8.62	[e]
			58.39	4.24	8.64	

[a] First line for each substance is calculated per cent; second found. [b] Analyses are for the crude products. [c] G. T. Morgan and J. D. Main Smith, *J. Chem. Soc.*, 920 (1926); m.p. 200°. [d] P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955); m.p. 288–289°. [e] P. Pfeiffer, E. Buchholz, and O. Bauer, *J. Prakt. Chem.*, **129**, 163 (1931); no m.p. reported.

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[2] A. S. Antsyshkina and M. A. Porai-Koshits, *Dokl. Akad. Nauk USSR*, **143**, 105 (1962); *Chem. Abstr.*, **57**, 2954*f* (1962).

Decomposition of the Electronically Excited Difluoramino Free Radical

Sir:

The ability of difluoramine to deaminate primary amines has been explained[1] by postulating the intermediate formation of fluorazene or fluoronitrene (NF). This intermediate species presumably arises by the loss of a fluoride ion from the initially formed unstable alkylammonium difluoramide.

We now have observed that photochemical activation (2537 Å.) of the difluoramino free radical[2] may also produce fluoronitrene by inducing loss of a fluorine radical. For example, irradiation of an equilibrium mixture of N_2F_4 and $\cdot NF_2$ at room temperature gave NF_3 and N_2F_2 along with N_2 and other products involving N_2F_2 decomposition in glass, N_2O, NO, and SiF_4.[3] Coupling of fluoronitrene can give rise to N_2F_2, a reaction which other nitrenes undergo,[4] and $F\cdot$ and $\cdot NF_2$ may combine to furnish NF_3. When SO_2 was introduced into the system (10 mmoles each of N_2F_4 and SO_2) a new compound, sulfuryl fluoride di-

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(1) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Am. Chem. Soc.*, **85**, 97 (1963).

(2) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

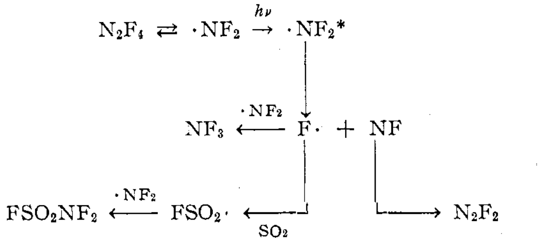
(3) C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *J. Am. Chem. Soc.*, **81**, 6397 (1959).

(4) G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961).

fluoramide, FSO_2NF_2, was formed in 89% yield together with N_2F_2 in 60% yield.[5] In addition small amounts of N_2O, NO, N_2, SiF_4, SOF_2, and SO_2F_2 were obtained.

Sulfuryl fluoride difluoramide was characterized by analysis (Found: N, 9.98, S, 22. 7), its infrared spectrum (bands at 6.72 and 8.0 μ, S=O, 10.0 and 10.87 μ, N–F, and 11.82 μ, S–F), molecular weight (Found: 135.7 mass spectrometrically, 136.2 by vapor density), n.m.r. (resonances at −1668 c.p.s.,[6] NF, and −984 c.p.s., S–F, in ratio of 2:1) and the mass spectrum.

These transformations are rationalized by the scheme



Although the formation of FSO_2NF_2 may be explained by assuming an initial attack on SO_2 by $\cdot NF_2$ with subsequent combination with $\cdot F$ or fluorine atom abstraction from N_2F_4, such a pathway does not seem reasonable in view of the known ability of $\cdot NF_2$ to act as an efficient radical trap.[7] Since SO_2F_2 was observed, but no bis-(difluoramino) derivative, fluorine radicals appear to lead the attack.[8] The scheme shown also may accommodate the observation that difluoramino sulfur pentafluoride is formed by irradiation of SF_4 and N_2F_4.[9]

Further work is in progress on the photochemistry of N_2F_4 and the chemistry of FSO_2NF_2.

Acknowledgments.—This investigation was supported by the Advanced Research Projects Agency under Army Ordnance Contract DA-01-021 ORD-11909. We are grateful to Mr. Kirt Keller and Mr. Floyd Hooper for technical assistance.

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(5) Based on the equation $N_2F_4 + SO_2 \rightarrow FSO_2NF_2 + {}^1/_2\, N_2F_2$.

(6) Referred to external $CFCl_3$. Samples measured neat at −50° using a 40 Mc. probe.

(7) J. P. Freeman, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p. 128.

(8) Also consistent with the present data is a sequence initiated by fluorine atom abstraction by an excited species, $\cdot NF_2^*$ or SO_2^*.

(9) A. L. Logothetis, G. N. Sausen, and R. J. Shozda, *Inorg. Chem.*, **2**, 173 (1963).

Book Reviews

Handbuch der Präparativen Anorganischen Chemie. Second Edition. Volume I. Edited by GEORG BRAUER. Ferdinand Enke Verlag, Stuttgart W. Hasenbergsteige 3, Germany, 1962. xiii + 884 pp. 15 × 25 cm. Price, DM. 124.

The First Edition of this compilation of inorganic preparations, which was published in a single volume in 1954, soon became a standard reference book for inorganic chemists. The extraordinary output of new inorganic compounds in the very recent past has necessitated the expansion of the Second Edition of this work to two volumes.

Volume I of the second edition contains contributions by 27 authors, each an authority in his field. The format is substantially the same as that of the First Edition. The volume opens with a section entitled "Preparative Methods" (111 pages) which consists of an excellent and fairly comprehensive discussion of the apparatus, materials, and techniques of importance in synthetic inorganic chemistry. This section is followed by 18 chapters dealing with the preparation of the representative elements and many of their compounds. The various chapter titles are: (1) Hydrogen, Deuterium, Water; (2) Hydrogen Peroxide; (3) Fluorine, Hydrogen Fluoride; (4) Fluorine Compounds; (5) Chlorine, Bromine, Iodine; (6) Oxygen, Ozone; (7) Sulfur, Selenium, Tellurium; (8) Nitrogen; (9) Phosphorus; (10) Arsenic, Antimony, Bismuth; (11) Carbon; (12) Silicon, Germanium; (13) Tin, Lead; (14) Boron; (15) Aluminum; (16) Gallium, Indium, Thallium; (17) Alkaline Earth Metals; (18) Alkali Metals.

The 18 chapters listed above include many preparations not found in the corresponding chapters of the First Edition. The nature of these new preparations reflects current research trends. For example, among the new substances found in the chapter on fluorine compounds are FSO_2NO, $PCl_4{\cdot}PF_6$, $(PNF_2)_3$, $(PNF_2)_4$, KPF_6, and ClF_3. In addition, an attempt has been made to incorporate newer and better methods for compounds included in the original edition, and compounds whose existence has been disproved, *e.g.*, OsF_8, have been deleted.

At the end of each preparation properties of the substance prepared and pertinent literature references are cited. To the reviewer, these lists of references appear to be comprehensive and up to date.

The directions for the various syntheses are, on the whole, given in a clear concise manner, and numerous (278) illustrations of apparatus are to be found. It is to be regretted, however, that actual quantities of reagents employed and yields of product obtained are not given in every instance.

A question will arise as to the reproducibility of the preparations described. On this point the reviewer can only cite his translation of the Editor's statement in the Preface to the effect that the preparations have been newly tested either in the laboratories of the authors or by exchange of experiences in different laboratories, and thus may be considered as reliably reproducible.

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