TABLE I

EQUILIBRATION OF cis- AND trans-4-
METHYLCYCLOHEXYLMERCURIC BROMIDES

Expt.	Solvent	Temp., °C.	Starting isomer	Method of analysis	% cis-	% trans.
1	Pyridine	95	trans-	Isolation of products	54	46
2	Pyridine	95	trans-	Infrared	52	48
3	Pyridine	95	cis-	Infrared	54	46

brating conditions, was cleaved stereospecifically with retention of configuration by mercuric bromide. The resulting mixture of cis- and trans-4-methylcyclohexylmercuric bromides contained an excess of the cis-isomer. Also the equilibration of the cis- and trans-4-methylcyclohexylmercuric bromides was carried out in dioxane at 98° using benzoyl peroxide as the catalyst. In these cases, greater decomposition occurred than in the equilibration in pyridine, product recovery being 65–70%. Again, the cis-isomer was present in greater concentration.

Although the present data do not permit an exact determination of the A value for the bromomercuri group, they indicate that the A value is approximately 0. This lack of a preference for an equatorial over an axial conformation probably is due, at least in part, to the long carbon–mercury bond and the high polarizability of the mercury atom, which minimize the a,a-1,3, bromomercuri group, hydrogen atom interactions. Eliel and Haber proposed that the relatively small equatorial preference of the bromo group (A = 0.73 kcal./mole) is due to a,a-1,3 London forces.[4] This type of attractive force, and more specific interactions, may be important with the bromomercuri group. The absence of a conformational preference for the bromomercuri group indicates that steric interactions are not necessarily directly related to the radii of the groups involved. The results presented here suggest that certain groups with large radii, such as the bromothallo group, may prefer the axial conformation.

(4) E. L. Eliel and R. G. Haber, THIS JOURNAL, 81, 1249 (1959).

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## THE FORMATION OF DINITROGEN TETRAFLUORIDE IN THE REACTION OF FLUORINE AND AMMONIA

Sir:

The preparation of dinitrogen tetrafluoride (N_2F_4) by the pyrolysis of nitrogen trifluoride over copper was reported recently.[1] We now wish to report the formation of this compound by the vapor phase reaction of fluorine and ammonia in a packed copper reactor.

Ruff and Hanke[2] investigated the vapor phase reaction of fluorine and ammonia in an unpacked copper reactor using both an excess of fluorine and of ammonia. The products in both cases were

(1) C. B. Colburn and A. Kennedy, THIS JOURNAL, 80, 5004 (1958).
(2) O. Ruff and E. Hanke, Z. anorg. u. allgem. Chem., 197, 394 (1931).

nitrogen trifluoride and ammonium fluoride (Equation 1), although the presence of other nitrogen fluorides was postulated.

$$4NH_3 + 3F_2 \longrightarrow NF_3 + 3NH_4F \qquad (1)$$
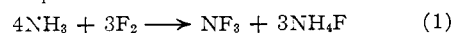
Yields of NF_3 were about 6%, based on the fluorine consumed. Evidently the ammonia was largely converted to nitrogen and hydrogen fluoride

$$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF \qquad (2)$$

We have reinvestigated this reaction in a packed T-shaped copper reactor, using both an excess of fluorine and of ammonia. Nitrogen was employed to dilute the reactants, and reaction proceeded smoothly with moderate evolution of heat. With excess fluorine, results paralleled Ruff's, although NF_3 yields were higher but, with excess ammonia, N_2F_4 also was obtained. The conditions employed are summarized in Table I.

TABLE I

REACTION CONDITIONS

	Excess F_2	Excess NH_3
Ammonia–fluorine ratio	1.1:1 (Stoichiometric = 1.33:1)	1.5:1 to 2.0:1
Nitrogen–fluorine ratio	5:1 to 20:1	5.0:1
Reactor packing	Copper shot or gauze	Copper gauze
Fluorine flow rate	1.3 to 2.5 liters/hr.	1.5 to 2.3 liters/hr.

The yields of NF_3 in the excess fluorine reaction were from 39 to 66% based on Equation 1. The combined product from a series of runs analyzed by mass spectral analysis had the composition: NF_3, 88.25%; CF_4, 9.40%; N_2O, 2.35%. The infrared spectrum agreed with a reference spectrum of NF_3.[3] (Carbon tetrafluoride probably was an impurity in the original fluorine.) Ammonium fluoride also was isolated and identified by chemical and infrared analysis.

In the excess ammonia reaction, unreacted ammonia was removed by water scrubbing or adsorbed on $CaCl_2$ or Linde molecular sieves. The gaseous products then were passed through a −78° trap and collected at −196°. Dinitrogen tetrafluoride was purified by removing more volatile impurities from a trap held at −142° (methylcyclopentane). The infrared spectrum of this purified fraction exhibited the same bands as reported by Colburn and Kennedy[1] and was virtually identical with that of a pure sample of N_2F_4 prepared in our laboratory by NF_3 pyrolysis. The band at 8.0 μ and the doublet at 8.92–8.97 μ are ascribed to C_2F_6 present in the original fluorine. Based on the fluorine converted to NF_3 and N_2F_4, the yields of N_2F_4 were as high as 11%, while NF_3 yields ranged from 6 to 24%.

The isolation of N_2F_4 and the higher yields of NF_3 obtained in our work are believed due, at least partly, to the use of a packed reactor. The copper packing reduces the intensity of the reaction and prevents the conversion of ammonia to nitrogen and hydrogen fluoride.

We wish to acknowledge the assistance of Mr. C. W. Schoenfelder in some phases of this work, and to thank Mr. L. Adlum for the infrared analyses,

(3) E. L. Pace and L. Pierce, J. Chem. Phys., 23, 1248 (1955).

and Mr. D. Y. Yee formerly of New York University for determining the mass spectrum of the nitrogen trifluoride sample. This work was supported by the Air Force under Contract No. AF33(616)-5222, Mr. Forrest Forbes, Project Engineer.

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MONASCORUBRIN. I. "MONASCAMINONE," A DEGRADATION PRODUCT

Sir:

Monascorubrin, first isolated by Nishikawa[1] from *Monascus purpureus* Wentii, belongs to the group of azaphilones[2] such as sclerotiorin[3] and rotiorin.[4] Monascorubrin, m.p. 134–136°, C_{23}-$H_{26}O_5$[5] (C, 72.2; H, 6.66), $[\alpha]^{16}_{700}$ $-1500°$ (c 0.1% in EtOH), C—CH_3 2.5, reacts with ammonia[6] to give monascamine,[7] m.p. 192°, $C_{23}H_{27}O_4N$ (C, 72.2; H, 6.93; N, 4.10), $[\alpha]^{16}_{700}$ $-2600°$ (c 0.125% in $CHCl_3$), which when treated with zinc in various media is converted into monascaminone (I),[8] m.p. 186°, $C_{22}H_{29}O_2N$ (C, 77.8; H, 8.50; N, 4.08), $[\alpha]_D$ 0°, λ^{EtOH}_{max} in mμ 253 (4.73), 302 (3.95) and 352 (3.78), ν^{KBr}_{max} in cm.$^{-1}$ 1710 (C=O).

Hydrogenation of I furnished dihydromonascaminone (II), m.p. 97–98°, λ^{EtOH}_{max} in mλ 239 (4.69), 288 (3.53) and 343 (3.69), ν^{KBr}_{max} 1717 cm.$^{-1}$ (C=O), and octahydromonascaminone (III), m.p. 181°, λ^{EtOH}_{max} in mμ 226 (3.90) and 282 (3.11). Thorough spectroscopic comparisons of II and derivatives with synthetic hydroxyisoquinolines established the nucleus to be 7-hydroxyisoquinoline.[9]

Beckmann rearrangement of monascaminone oxime, m.p. 211°, gave *n*-heptylamine. Treatment of I with sodium borohydride afforded monascaminol (IV), m.p. 196–197°, $C_{22}H_{31}O_2N$ (C, 77.1; H, 9.10; N, 4.31), λ^{MeOH}_{max} in mμ 256 (4.80), 307 (3.88) and 352 (3.77), which when heated in polyphosphoric acid at 150° gave dehydromonascaminol (V), m. 192–3°, $C_{22}H_{29}ON$ (C, 81.3; H, 9.34), λ^{EtOH}_{max} in mμ 225 (4.33), 262 (4.59), 318 (3.75) and 352 (3.69). The infrared peak at 1710 cm.$^{-1}$ in I, and comparisons of the ultraviolet peaks of IV and V with I demonstrate that the *n*-heptoyl chain must be attached to the aromatic nucleus through one saturated carbon atom. Permanganate oxidation of I afforded pyridine-1,3-4-tricarboxylic acid. Ozonolysis of O-acetylmonascaminone, m.p. 76–79°, gave acetaldehyde, and subsequent hydrogen peroxide oxidation of the nonvolatile ozonolysis product furnished an acid, m.p.

(1) H. Nishikawa, *J. Agr. Chem. Soc Japan*, **5**, 1007 (1932).

(2) A. D. G. Powell, A. Robertson and W. B. Whalley, *Chem. Soc.*, Special Publ., No. 5, 27 (1956).

(3) G. B. Jackman, A. Robertson, R. B. Travers and W. B. Whalley, *J. Chem. Soc.*, 1814 (1958); J. H. Birkinshaw and P. Chaplen, *Biochem. J.*, **69**, 505 (1958); H. Watanabe, *J. Pharm. Soc. Japan*, **72**, 807 (1952); Y. Yamamoto and N. Nishikawa, *ibid.*, **79**, 297 (1959).

(4) G. B. Jackman, A Robertson, R. B. Travers and W. B. Whalley, *J. Chem. Soc.*, 1825 (1958).

(5) Analyses of monascorubrin and derivatives also agree with the $C_{22}H_{24}O_5$ formula adopted by Nishikawa[1] and Powell, *et al.*[2]

(6) Hence the name azaphilones.

(7) Also a fungal metabolite; described as monascorubramine in reference 2.

(8) Described as dideoxymonascorubramine in reference 2.

(9) These results will be reported elsewhere in detail.

240°, $C_{22}H_{27}O_5N$ (C, 68.1; H, 7.06; N, 3.20), which gave an intense orange color with ferrous sulfate.[10] Accordingly, a propenyl group is attached to C-3. The C-8 position should be vacant because of the positive diazo coupling reactions of I and derivatives. Taking into account the presence of three C—CH_3 groups in monascaminone, these results can be expressed by the partial structure I, and evidence to extend this to VI was provided by structure considerations of monascorubrin (following communication).
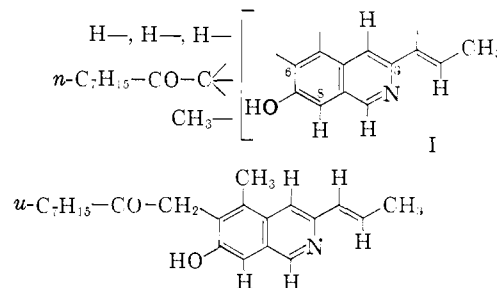
(10) H. Ley, Chr. Schwarte and O. Münnich, *Ber.*, **57**, 349 (1924).

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MONASCORUBRIN. II.[1] STRUCTURES OF MONASCORUBRIN AND MONASCAMINE

Sir:

Probable structures I and II are assigned to monascorubrin and monascamine, respectively, and the partial structure of monascaminone (III)[1] is completed. Comparisons of the ultraviolet and infrared (1600–1500 cm.$^{-1}$ skeletal stretching region) of I and II and their dihydro derivatives suggested that the conversion involved was merely an exchange of –O– for –NH–. Furthermore, production of III under various conditions indicated the absence of skeletal rearrangements, and thus the framework of III is retained in I and II. The five-membered lactone[2] and ke-

TABLE I

INFRARED CARBONYL BANDS, CM.$^{-1}$

Monascorubrin (I) (CCl_4)	1759	1729
Monascamine (II) (CCl_4)	1734	1705
Monascamine-HCl (KBr)	1745	1718
N-Methylmonascamine (CCl_4)	1733	1712
Tetrabromomonascamine[2] (KBr)	1796	1742
Secomonascamine (IV) (KBr)	1703	
Tetrabromosecomonascamine[2] (KBr)	1795	1742
Secomonascamine·HCl, Form A (Nujol)	1715	
Form B (KBr)	1745	1725

(1) Paper I, preceding communication.

(2) Though definite structures cannot yet be assigned to tetrabromomonascamine, m.p. 88–91°, $C_{21}H_{25}O_4NBr_4$, and tetrabromosecomonascamine, m.p. 138–140°, $C_{21}H_{27}O_4NBr_4$, their infrared spectra serve to demonstrate the presence of an α-bromo-γ-lactone. The lactone is lost as carbon dioxide during the conversion of II to III.