some differences have already been noted.[1] The esr results, based on an eigenvector property of a single species, may actually be a more trustworthy measure of the electronic effect of a substituent than a $\sigma$ constant based on differences between two species. To illustrate, in all but one of the systems of Table II, the *p*-F substituent is found to be slightly electron supplying. The $\sigma$ constant classifies this substituent as slightly electron withdrawing. Recently, Birchall and Jolly[23] concluded from ionization constants of substituted anilines in anhydrous ammonia that *p*-F was electron supplying and the $\sigma$ value should be $-0.05$ in systems where direct resonance effects are possible rather than 0.006. We intend to study substituent effects in other systems, paying particular attention to the "ill-behaved" substituents.

## Experimental Section

The nitrosobenzenes were a gift of Dr. Travis Stevens (Redstone Arsenal). Solutions 0.1 *M* in the nitrosobenzene were deoxygenated in the degassing apparatus previously described.[24] The solvent was reagent grade benzene. Prior to irradiation many of the solutions contained small concentrations of radical which appeared to be the monophenyl nitroxide. Trace amounts of phenylhydroxyamine impurity could give rise to this radical *via* reaction VII. This reaction has been shown to occur in solution.[25] On irradiation these trace radicals were swamped by the characteristic diaryl nitroxide triplet.

$$\mathrm{PhNHOH} + \mathrm{PhNO} \rightleftharpoons 2\mathrm{PhNHO}\cdot$$
VII

The ultraviolet source was a Bausch and Lomb SP 200-w. super pressure Hg lamp. Spectra were measured with a Varian V-4500 epr spectrometer equipped with a 9-in. magnet. Sweep rates were calibrated by the spectrum of *p*-benzosemiquinone in aqueous ethanol.[26] Spectra were solved by standard means.

**Registry No.**—VI (R = *p*-$NO_2$), 3313-75-5; VI (R = *p*-COOMe), 14210-54-9; VI (R = *p*-$CO_2$Et), 14210-55-0; VI (R = *m*-$NO_2$), 14210-56-1; VI (R = *m*-F), 14210-57-2; VI (R = *m*-Cl), 14210-58-3; VI (R = *p*-Br), 14210-59-4; VI (R = *p*-Cl), 14210-60-7; VI (R = *m*-$CO_2$Me), 14320-17-3; VI (R = *p*-H), 712-51-6; VI (R = *p*-F), 14210-62-9; VI (R = *p*-$CH_3$), 720-45-6; VI (R = *p*-$OCH_3$), 2643-00-7.

**Acknowledgments.**—We are grateful to Dr. Travis Stevens for his generous gift of the starting materials and to Dr. Brinkley Snowden, Jr., for writing a program to calculate correlation coefficients and least-squares slopes. We thank Dr. Edward G. Janzen for his helpful discussions and permission to cite his unpublished work.

(23) T. Birchall and W. L. Jolly, *J. Am. Chem. Soc.*, **88**, 5439 (1966).
(24) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).
(25) G. A. Russell and E. J. Geels, *ibid.*, **87**, 122 (1965).
(26) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

# Electron Impact Induced Methyl Migration in Dimethylamino Heteroaromatic Systems[1a,b]

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The syntheses of 2-dimethylamino-5-nitropyrimidine (Ia), 2-di(trideuteriomethyl)amino-5-nitropyrimidine (Ib), and 2-dimethylamino-5-benzenesulfonamidopyrimidine (III) are reported. The mass spectra of Ia, Ib, III, and 6-dimethylaminopurine (II) are analyzed. Intense peaks M − 29 found in the spectra of Ia and II are shown to be due to loss of $CH_3N$ from the molecular ion. This fragmentation is presumably accompanied by methyl migration from the *exo*- to the *endo*-cyclic nitrogen.

Considerable attention has been paid to electron impact induced rearrangements involving groups other than hydrogen after the first cases of such fragmentation processes had been reported.[2] Recently, many cases have been reported in which alkyl or aryl groups migrated under electron impact from a carbon atom to another carbon[3] or to a nitrogen[4] atom in the molecular ion or from a heteroatom to a carbon atom[5] or from one heteroatom to another.[6] We wish to report a new case in which, under electron impact, a methyl group was found to migrate from a nitrogen atom probably to another nitrogen atom in the molecular ion.

In a mass spectral investigation of some substituted purines, an intense ($\%\Sigma_{40}$ 9.5) M − 29 peak was found in the mass spectrum of 6-dimethylaminopurine (II) (Figure 1). A similar M − 29 peak was also intense ($\%\Sigma_{40}$ 6.6) in the mass spectrum of 2-dimethylamino-5-nitropyrimidine (Ia) (Figure 2). The corresponding metastable peaks were detected in both cases (see

(1) (a) This investigation was supported by Grant GB-1806 from the University to M.S. (b) Part VIII in Studies in Mass Spectrometry. Part VII: J. Sharvit and A. Mandelbaum, *Israel J. Chem.*, **5**, 33 (1967). (c) Bar-Ilan University. (d) Israel Institute of Technology.

(2) (a) P. Funke, K. G. Das, and A. K. Bose, *J. Am. Chem. Soc.*, **86**, 2527 (1964); (b) A. Mandelbaum and M. Cais, *Tetrahedron Letters*, 3847 (1964); (c) F. Komitsky, J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 1398 (1965).

(3) (a) C. Djerassi, A. M. Duffield, F. Komitsky, and L. Tokes, *ibid.*, **87**, 860 (1965); (b) H. E. Audier, J. F. Dugin, M. Fetizon, and Y. Hoppilliard, *Tetrahedron Letters*, 2077 (1966); (c) R. A. W. Johnstone and B. J. Millard, *Z. Naturforsch.*, **21a**, 604 (1966); (d) J. Baldas and Q. N. Porter, *Chem. Commun.*, 511 (1966); (e) J. H. Bouse, R. G. Cooks, S-O. Lawesson, P. Jakobsen, and G. Schroll, *ibid.*, 539 (1966).

(4) (a) B. R. Webster, *ibid.*, 124 (1966); (b) R. M. Moriarty and A. M. Kirkien-Konasiewicz, *Tetrahedron Letters*, 4123 (1966); (c) A. Bhatti, R. A. N. Johnstone, and B. J. Millard, *J. Chem. Soc., Sect. C*, 358 (1966).

(5) (a) A. Tatematsu, S. Inoue, and T. Goto, *Tetrahedron Letters*, 4609 (1966); (b) J. L. Occolowitz and J. M. Swan, *Australian J. Chem.*, **19**, 1187 (1966); (c) M. Fischer and C. Djerassi, *Chem. Ber.*, **99**, 750 (1966);

(6) (a) P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, **88**, 2469 (1966); (b) J. H. Bowie, R. Grigg, S-O. Lawesson, P. Madsen, G. Schroll, and D. H. Williams, *ibid.*, **88**, 1699 (1966); (c) O. L. Chapman, T. H. Kinstle, and M. T. Sung, *ibid.*, **88**, 2618 (1966); (d) J. Silbiger, C. Lifschitz, J. Fuchs, and A. Mandelbaum, *ibid.*, **89**, 4308 (1967); (e) M. F. Grostic, R. J. Wnuk, and F. A. MacKellar, *ibid.*, **88**, 4664 (1966); (f) M. J. Rix, A. J. C. Wakefield, and B. R. Webster, *Chem. Commun.*, 748 (1966); (g) R. T. Aplin, J. H. Jones, and B. Liberek, *ibid.*, 794 (1966).

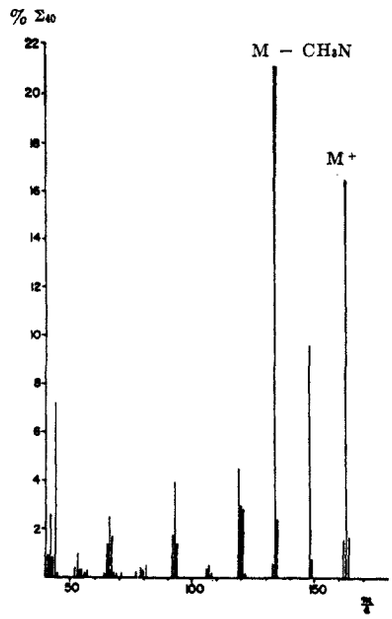



Figure 1.—Mass spectrum of II.

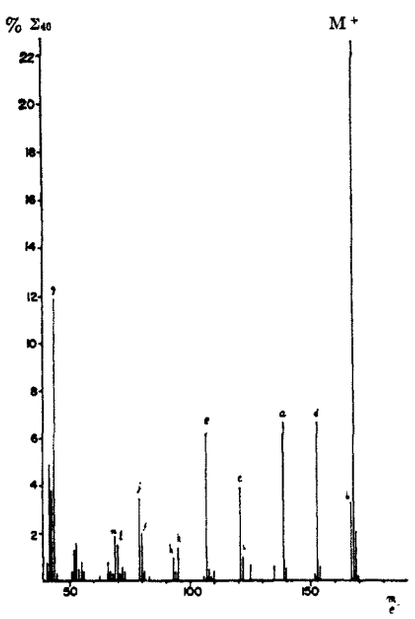
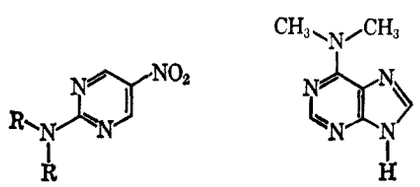



Figure 2.—Mass spectrum of Ia.




Ia, R = $CH_3$
b, R = $CD_3$

II

Tables I and II). Only two possible compositions exist for the neutral fragment that is lost from the molecular ion in these two cases, namely, $C_2H_5$ and $CH_3N$. In the mass spectrum of 2-di(trideuteriomethyl)amino-5-nitropyrimidine (Ib), this peak was shifted to 142 (M − 32), indicating that only one methyl group is involved in this rearrangement. Since we have found peak M − 29 to be of very low intensity in homocyclic aromatic dimethylamines (*e.g.*, dimethylaniline, dimethylnaphthylamines), we assume that one methyl group migrates from the nitrogen atom to which it was originally attached to a nitrogen atom of the heterocyclic system. This process can be visualized in the mechanism suggested by eq 1.

TABLE I

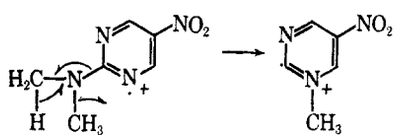
METASTABLE TRANSITIONS OF 2-DIMETHYLAMINO-5-NITROPYRIMIDINE (Ia) AND ITS HEXADEUTERIO DERIVATIVE (Ib)

| Ia | | | Ib | | |
|---|---|---|---|---|---|
| Transition | Found | Calcd | Transition | Found | Calcd |
| 168 → 139 | 115.0 | 115.0 | 174 → 142 | 115.8 | 115.9 |
| 167 → 121 | 87.7 | 87.6 | 172 → 126 | 92.2 | 92.3 |
| 153 → 107 | 75.0 | 74.9 | 156 → 110 | 77.6 | 77.5 |
| 107 → 80 | 60.0 | 59.8 | | | |

TABLE II

METASTABLE TRANSITIONS OF 6-DIMETHYLAMINOPURINE (II)

| Transition | Found | Calcd |
|---|---|---|
| 163 → 134 | 110.0 | 110.1 |
| 148 → 121 | 99.0 | 99.0 |
| 120 → 93 | 72.2 | 72.1 |




(1)

ion a

The availability of the deuterated compound Ib made it possible to investigate the origin of other peaks in the mass spectrum of Ia. The suggested fragmentation pattern is summarized in Scheme I. The *m/e* 167 peak (M − 1) was in great part (67%) shifted to *m/e* 172, leading to the conclusion that most of M − 1 ions are formed by the loss of a hydrogen atom from the methyl groups. The *m/e* 121 peak was completely shifted to *m/e* 126. A metastable peak at *m/e* 87.7 (see Table I) supports process suggested by eq 2 (see

$$\text{ion b} \xrightarrow{-NO_2} \text{ion c} \qquad (2)$$

Scheme I). The *m/e* 153 ion d (shifted to 156 in Ib) is formed by the loss of one methyl group from the molecular ion. This ion d loses the $NO_2$ group leading to *m/e* 107 (shifted to 110) ion e. The ion e can give rise to *m/e* 80 (shifted to 83) ion f by elimination of HCN.[7] These fragmentations are supported by metastable peaks (see Table I).

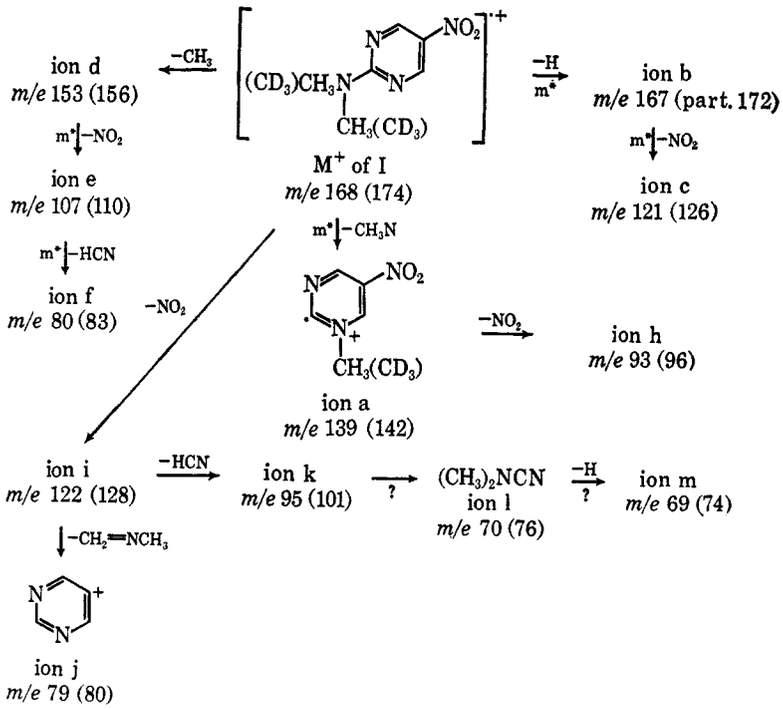
The formation of other ions can be explained as shown in Scheme I on the basis of shifts of the corresponding peaks in the deuterated compound Ib. No corresponding metastable transitions were detected. The concurrent presence of nitro and dimethylamino groups seems to suppress the opening of the heterocyclic ring and the loss of HCN is responsible for only a small part of the total ion current.[7,8]

An interesting contrast to the fragmentations of I and II was found in the case of 2-dimethylamino-5-benzenesulfonamidopyrimidine (III) (Scheme II). Here the primary fragmentation is loss of a benzenesulfinyl radical (141 mass units) to give the stabilized ion n (*m/e* 137) whose peak is by far the largest in the mass

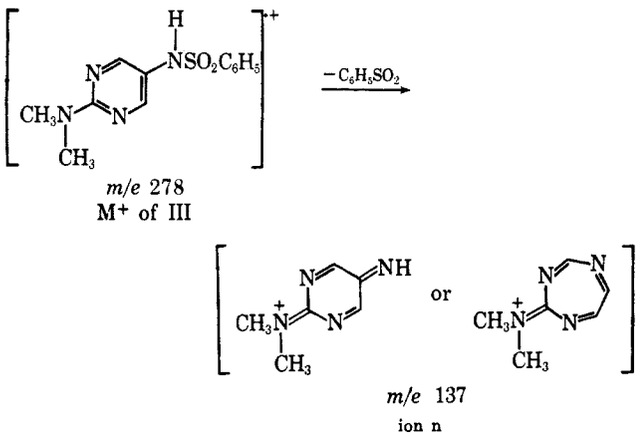
(7) J. M. Rice, G. O. Dudek, and M. Barber, *J. Am. Chem. Soc.*, **87**, 4569 (1965).

(8) T. Nishiwaki, *Tetrahedron*, **22**, 3117 (1966).

SCHEME I




SCHEME II




spectrum ($\%\Sigma_{40}$ 48.7) (see Figure 3). Single canonical forms of alternative structures for ion n are shown in Scheme II. The further breakdown of ion n by loss of HCN is confirmed by the presence of a metastable peak at 88.4 (calcd for 137 → 110: 88.3).

In part, ion n appears also to fragment to ion *m/e* 94 by loss of $CH_3N{=}CH_2$. Be it noted, however, that neither the molecular ion of III nor the derivative ion n show a loss of a neutral fragment of 29 mass units ($CH_2{=}NH$). Another example of directive influence on fragmentation pattern is thus presented.

## Syntheses

2-Dimethylamino-5-nitropyrimidine (Ia) has been previously prepared by Waletzky[9] by the reaction of dimethylamine with 2-chloro-5-nitropyrimidine. We found it more convenient to prepare Ia by an unequivocal "principle synthesis" [10] using 1,1-dimethylaguanidine and sodium nitromalonaldehyde.[11,12] Considerations of economy made it desirable to synthesize the labled compound, Ib, by an appropriate deuteriomethylation of 2-amino-5-nitropyrimidine[11] with deuteriomethyl iodide. It is well known[10,13] that the reaction of other 2-aminopyrimidines with methyl iodide under neutral conditions results in methylation of a ring nitrogen rather than the exocyclic one.[14] In the case of 2-amino-5-nitropyrimidine, however, even such ring alkylation was not feaseable.[13] In contrast, it has been reported[12,15] that reaction of methyl iodide with the *anions* of 2-aminopyrimidines results in alkylation of the *exocyclic* nitrogen.[16] The formation of the anion of 2-amino-5-nitropyrimidine is a particularly favorable process owing to the presence of the nitro group *para* to the amino group.

In this case it was found that 2-amino-5-nitropyrimidine reacted smoothly with 2 equiv of sodium hydride and 2 equiv of methyl iodide (or trideuteriomethyl iodide) to give high yields of Ia (or Ib).

The product thus obtained was identical with authentic Ia obtained by the above-mentioned "principle

(9) E. Waletzky, U. S. Patent 2,543,748 (March 6, 1951); *Chem. Abstr.*, **45**, 5371*d* (1961).

(10) D. Brown, "The Pyrimidines," Interscience Publishers, Inc., New York, N. Y., 1962.

(11) W. J. Hale and H. C. Brill, *J. Am. Chem. Soc.*, **34**, 82 (1912).

(12) C. G. Overberger and I. C. Kogan, *ibid.*, **76**, 1065 (1954).

(13) D. J. Brown and J. S. Harper, *J. Chem. Soc.*, 1276 (1963).

(14) The latter process would involve localization of the previously delocalized lone electron pair of the exocyclic nitrogen, as well as creation of a localized formal positive charge, whereas ring-nitrogen methylation presumably involves nucleophilic displacement by the electron pair which is in any case localized in a nitrogen $sp^2$ orbital, while the formal positive charge being created is distributed over both the ring and the exocyclic nitrogens.

(15) R. C. Adams and F. C. Whitmore, *J. Am. Chem. Soc.*, **67**, 735 (1945).

(16) The anion IV has a localized ($sp^2$) electron pair both on the exocyclic and the endocyclic nitrogens. Nucleophilic displacement by the electron pair on the exocyclic nitrogen is preferred since it can occur with preservation of "aromaticity" of the ring without charge separation. It should be noted that in aminopyrimidines the "aromatic" amino tautomer is of lower energy than the imino tautomer. This discussion is not inconsistent with the recently reported finding of G. C. Hopkins, J. P. Jonak, H. Tieckelmann, and H. J. Minnemeyer [*J. Org. Chem.*, **31**, 3969 (1966)] that the anions of 2-hydroxypyrimidines are alkylated preferentially on the ring nitrogen rather than the exocyclic oxygen. For not only is nitrogen more nucleophilic than an analogous oxygen, but also, in "2-hydroxypyrimidines," the oxo tautomer is of lower energy than the "aromatic" hydroxy tautomer.

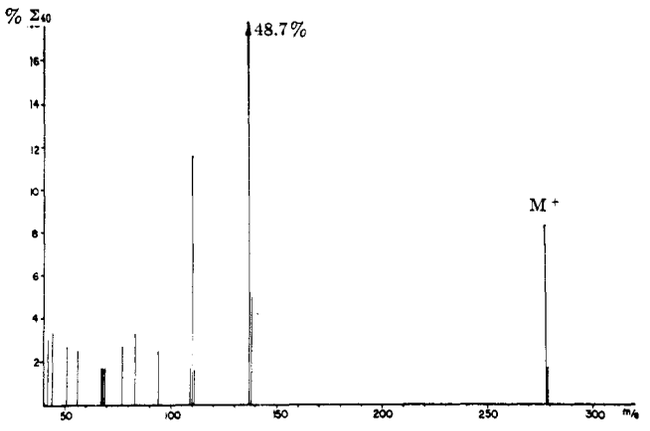
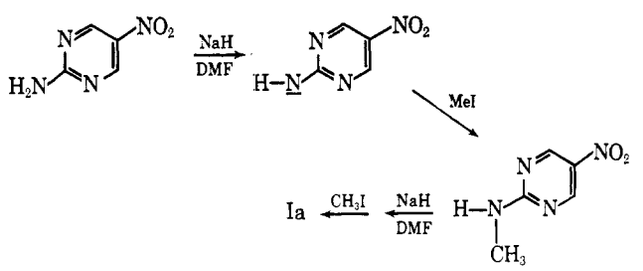



Figure 3.—Mass spectrum of III.

synthesis," proving that methylation of the exocyclic nitrogen had occurred (Scheme III).

SCHEME III




The synthesis of III was readily accomplished by the catalytic reduction of Ia to 5-amino-2-dimethylaminopyrimidine and reaction of the latter with benzenesulfonyl chloride in pyridine solution.

## Experimental Section

Spectra were taken on an Atlas $CH_4$ mass spectrometer at an ionization potential of 70 ev and ionizing current of 20 $\mu$a. Samples were introduced by the direct inlet system. Melting points were determined on a Fischer hot stage and are uncorrected. Thin layer chromatography (tlc) was carried out on fluorescent silica gel ($D_5F$-Fluka).

**6-Dimethylaminopurine** (II) was obtained from "Calbiochem," Los Angeles, Calif., and is their "Grade A."

**2-Dimethylamino-5-nitropyrimidine (Ia). Method A.**—A solution of 8.4 g (31 mmoles) of 1,1-dimethylguanidine sulfate, 5 g (31 mmoles) of sodium nitromalonaldehyde,[17] 3.2 g (31 mmoles) of sodium carbonate, and a few drops of piperidine in 35 ml of water was allowed to stand at ambient temperatures. The precipitate was collected, dried, and subjected to Soxhlet extraction with benzene. A 33% yield (1.73 g) of light yellow needles, sensitive to air and light, was obtained: mp 222° (lit.[9] mp 222°); tlc, $R_f$ 0.60 using methanol–benzene (1:9, v/v); $\lambda_{max}^{MeOH}$ 223 m$\mu$ ($\epsilon$ 7000), 345 (14,300).

**Method B.**—2-Amino-5-nitropyrimidine (0.5 g, 3.5 mmoles) was added with stirring and in a dry nitrogen atmosphere to a suspension of 0.168 (7 mmoles) of sodium hydride (a 50% suspension in mineral oil was used) in 10 ml of dimethylformamide. After the reaction subsided, 0.99 g (7 mmoles) of methyl iodide was added and stirring was continued for 24 hr. The solvent was removed *in vacuo* and the residue rinsed with pentane to remove mineral oil and with 8 ml water to remove sodium iodide. Crystallization from methanol yielded 0.49 g (85%) of light yellow needles of IIa, identical in all respects with the product obtained by method A.

**2-Di(trideuteriomethyl)amino-5-nitropyrimidine** (Ib) was prepared by method B using 7 mmoles of $CD_3I$ (obtained from Yeda Inc., Rehovot, Israel).

**2-Dimethylamino-5-benzenesulfonamidopyrimidine** (III).—A suspension of 0.35 g (2.1 mmoles) of 2-dimethylamino-5-nitropyrimidine[11] in 100 ml of methanol was hydrogenated catalytically in a Parr low-pressure hydrogenation apparatus, using 0.1 g of platinum oxide. The catalyst was removed by filtration and the solvent evaporated under reduced pressure. The 5-amino-2-dimethylaminopyrimidine thus obtained (tlc, $R_f$ 0.52 using isopropyl alcohol–benzene, 1:1, v/v) was very sensitive to air oxidation and was therefore immediately thoroughly dried under vacuum (oil pump), dissolved in 10 ml of dry pyridine (under nitrogen), and treated with 0.5 g of benzenesulfonyl chloride. The mixture was stirred at ambient temperatures for 3.5 hr. After partial removal of solvent under vacuum (oil pump), the product was precipitated by the addition of ice water and adjustment of pH to 6. The product was collected, washed with cold water, dried, and recrystallized from methanol: yield, 0.3 g (60%); mp 178°; tlc, $R_f$ 0.72 using isopropyl alcohol–benzene (1:1, v/v); $\lambda_{max}^{MeOH}$ 224 m$\mu$ ($\epsilon$ 9900), 257 (19,100), 332 (1800).

*Anal.* Calcd for $C_{12}H_{14}N_4SO_2$: C, 51.79; H, 5.07; N, 20.14; S, 11.50. Found: C, 52.01; H, 5.16; N, 20.39; S, 11.68.

**Registry No.**—Ia, 14233-44-4; Ib, 14233-45-5; II, 1128-06-7; III, 14233-47-7.

(17) P. E. Fanta, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 844.

# Organic Fluoronitrogens. VII.[1a] Tris(difluoramino)fluoromethane and Related Compounds[1b]

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The direct fluorination of guanylurea sulfate yields tris(difluoramino)fluoromethane (II), pentafluoroguanidine (III), tetrafluoroformamidine (IV), 3,3-bis(difluoramino)perfluoro-2-azapropionyl fluoride (V), bis(difluoramino)-fluoromethyl isocyanate (VI), and the previously described bis(difluoramino)difluoromethane (I). The fluorination of guanylurea yields I–IV. Some of the physical and chemical properties of these nitrogen–fluorine compounds are presented. The compounds, especially II–IV, are shock sensitive and explosive.

The synthesis of bis(difluoramino)difluoromethane (I), the first reported compound having more than one difluoramino group bonded to a single carbon atom, was recently disclosed in a previous paper[2] in this series and by Englin and co-workers.[3] This paper describes the direct fluorination of guanylurea and guanylurea sulfate which resulted in the synthesis

(1) (a) Preceding paper in this series: R. L. Rebertus, J. J. McBrady, and J. G. Gagnon, *J. Org. Chem.*, **32**, 1944 (1967). (b) Presented in part at the International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967. Note: Pentafluoroguanidine was also prepared by another route which was very recently reported by R. A. Davis, J. L. Kroon, and D. A. Rausch, *J. Org. Chem.*, **32**, 1662 (1967). (c) Deceased, Aug 5, 1965.

(2) R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *J. Org. Chem.*, **31**, 4232 (1966).

(3) M. A. Englin, S. P. Makarov, S. S. Dubov, and A. Ya. Yakubovich, *Zh. Obshch. Khim.*, **35**, 1416 (1965).