Products of Rearrangement of *m*-Chloro-*N*-nitro-*N*-methylaniline[1]

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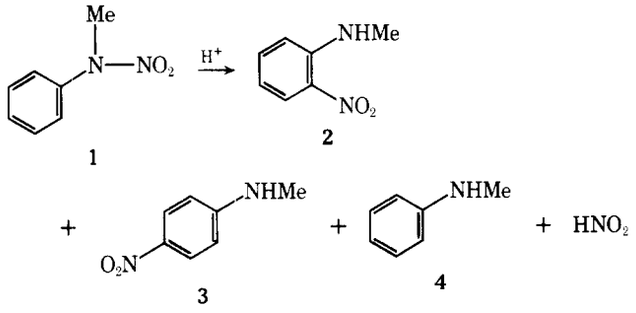
The rearrangement of aromatic nitramines is exemplified by the isomerization of *N*-nitro-*N*-methylaniline[3] (**1**). The



reaction has been found to be at least partially intramolecular.[4] In spite of the apparent simplicity of this reaction, there is considerable disagreement regarding its intimate nature. Three different mechanisms have been proposed by different research groups to account for the results (Chart I). (1) The "cartwheel" mechanism[5] supposes that the protonated nitramine isomerizes to a nitritoamine (>NON=O) which then undergoes a Claisen-like rearrangement to an ortho *C*-nitrite intermediate. The latter can undergo further rearrangement to a para *C*-nitrite intermediate. It is suggested that either of the *C*-nitrites can isomerize to *C*-nitro compounds identical with those expected in nitration. (2) The π complex mechanism[6,7] proposes that the protonated nitramine breaks down to form a π complex of the type postulated in aromatic nitration. The remaining steps to product are analogous to those suggested for the latter reaction. (3) The cation radical mechanism[8,9] involves symmetrical N–N bond scission in the protonated nitramine to yield a pair of radicals—anilinium cation radical and nitrogen dioxide—which can recombine at the ortho and para positions of the ring to form the same nitration intermediates common to the other two mechanisms.

Because of the proposed similarity between the "cartwheel" mechanism and the Claisen rearrangement, it was anticipated that similar factors should control the product distribution in both migrations, if this mechanism was valid. On the other hand, the other two mechanisms would predict a more or less statistical distribution of products depending on the strength of binding between the ring and the dissociated nitro group. Since the product distribution in the Claisen rearrangement of allyl *m*-chlorophenyl ether (**4**) has been accurately determined,[10] it was decided to investigate the products formed in acid-catalyzed reaction of *m*-chloro-*N*-nitro-*N*-methylaniline (**5**) and compare the results with those from the Claisen rearrangement.

Results and Discussion

The products of acid-catalyzed rearrangement of *m*-chloro-*N*-nitro-*N*-methylaniline (**5**) were determined by isotope dilution analysis with the results shown in Table I. This analysis accounts for about 98% of the aromatic portion of the original nitramine and for about 85% of the nitro group. Nitrous acid was detected in the reaction mixture but its concentration was not determined; it probably is the principal form in which the remainder of the nitro group appears in the product. About 50% of the product corresponds to ortho rearrangement (**8** + **11**), 35% to para migration (**9**), and 13% to denitration (**6**). These figures are surprisingly close to those obtained for *N*-nitro-*N*-methylaniline,[3] for which there was about 49% ortho rearrangement, 32% of para isomerization, and 10% of denitration. It is especially noteworthy that there is no evidence for meta rearrangement in either case, which implies that the intermediates in the rearrangement process do not resemble those in direct nitration and that the rearrangement mechanism must specifically prohibit meta nitro compound formation.

As mentioned above, the "cartwheel" mechanism bears a superficial resemblance to the Claisen rearrangement. However, the product distribution from the nitramine (**5**) does not at all resemble that from rearrangement of the allyl ether (**4**).[10] The allyl ether provides no para-substituted isomer as does the nitramine. Furthermore, the ratio of the ortho products formed in the two processes is quite different. The nitramine rearrangement gives a ratio of 2 substitution to 6 substitution of 0.57 while the Claisen rearrangement yields the two isomers in a ratio of 1.92. Thus, any relation between the Claisen and nitramine rearrangements must not extend to product determination.

The distribution of isomers resulting from the acid-catalyzed reaction of **5** is approximately that expected from a model in which the nitro group is relatively unrestricted by the aromatic portion of the system. If it is assumed that the variations in percentages of position isomers produced in the

Chart I

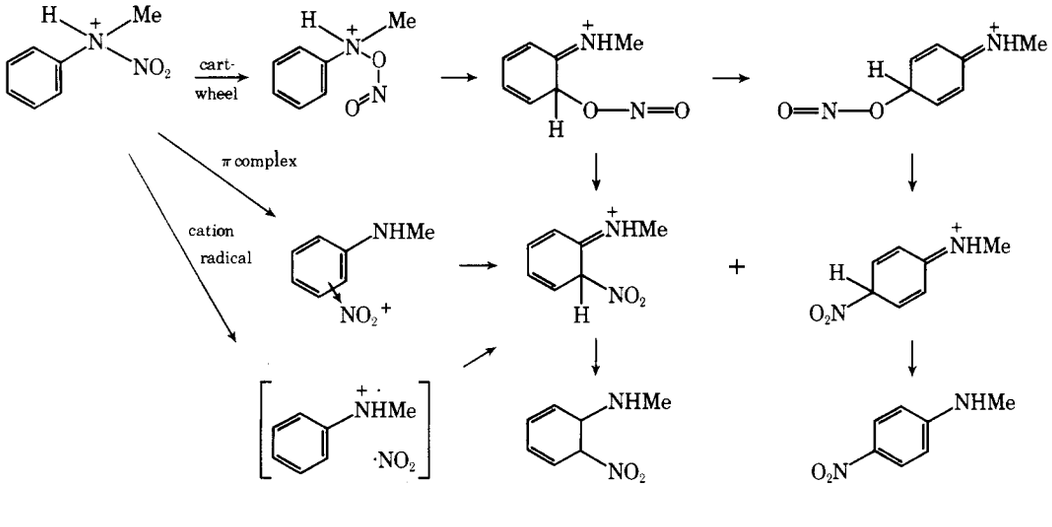


Table I. Rearrangement Products of *m*-Chloro-*N*-nitro-*N*-methylaniline (5)[a]

Product	% yield
3-Chloro-*N*-methylaniline (**6**)	13.4 ± 0.4
3-Nitro-*N*-methylaniline (**7**)	0.0 ± 0.0
3-Chloro-2-nitro-*N*-methylaniline (**8**)	18.1 ± 0.4
3-Chloro-4-nitro-*N*-methylaniline (**9**)	34.8 ± 0.1
3-Chloro-5-nitro-*N*-methylaniline (**10**)	0.0 ± 0.0
3-Chloro-6-nitro-*N*-methylaniline[b] (**11**)	31.6 ± 0.7

[a] Catalyzed by 0.501 M $HClO_4$ in 1:50 dioxane–water, temperature 55 °C. [b] More properly this is named 5-chloro-2-nitro-*N*-methylaniline. However, the name used in this table emphasizes the interrelations between the isomers.

rearrangements of *N*-nitro-*N*-methylaniline and **5** are due only to the steric effects of the methylamino and chloro groups interfering with an incoming nitro group, it is possible to assign parameters that permit the estimation of the amount of each isomer formed. Thus, the amount of substitution at one ortho position in the *N*-methylaniline moiety (in the rearrangement of *N*-nitro-*N*-methylaniline) is 0.77 (½ of 49%/32%) of that at the unencumbered para position. If this same figure applies to substitution at the 6 position in the *m*-chloro-*N*-methylaniline fragment, the observed product distribution requires 0.84 (0.77 × 35%/32%) for the 4 position (this represents the steric effect for substitution ortho to a chloro group as compared to an unhindered position). The 2 position in the *m*-chloro-*N*-methylaniline system is flanked by both a methylamino and a chloro group so the steric factor for this site should be the product of 0.77 and 0.84 (or 0.65). The numbers lead to the prediction that the *nitrated product* formed in the isomerization of **5** should consist of 29% of the 2 isomer, 37% of the 4 isomer, and 34% of the 6 isomer (100% total). The actual experimental values are 21, 41, and 38%, respectively. Better agreement would be obtained if the entirely reasonable assumption was made that the combined steric effects of the methylamino and chloro groups acting in concert on the 2 position were greater in magnitude than that predicted by taking the product of the steric effects of the groups acting separately on the 6 and the 4 positions, respectively (in fact, exact reproduction of the experimental data is possible if it is assumed that when both groups are simultaneously involved, their individual steric effects are 25% greater than when they function separately). In any case, the predicted and experimental values are in sufficient agreement to support the contention that, at some point in the reaction, the nitro group is weakly bound, if at all, to the anilino system so that its subsequent attachment to the ring at the ortho and para positions must be relatively random.

The "cartwheel" mechanism of the nitramine rearrangement involves firm attachment of the nitro group first to the ortho position(s) and then to the para position. Unless the three isomeric intermediates are in equilibrium, which seems unlikely because of their chemical fragility, the "cartwheel" mechanism is not capable of accommodating the experimental information that isomer formation, except for a small steric effect and the requirement for ortho, para substitution, is random. On the other hand, these findings can be interpreted in terms of either the π-complex or radical cation mechanisms since in either of these pathways the nitro group is probably rather loosely associated with the ring system.

Experimental Section

Preparation of *m*-Chloro-*N*-nitro-*N*-methylaniline-^{14}C. A. *m*-Dinitrobenzene-^{14}C. A cold solution of 45.0 ml of concentrated sulfuric acid and 45.0 ml of concentrated nitric acid was added in small portions with swirling and intermittent cooling to 17.25 g (0.221 mol) of benzene-^{14}C. Then 90 ml of concentrated sulfuric acid was added in small portions. The mixture was heated to 120 °C, cooled to 80 °C, and poured into 1500 ml of cold water. The product was collected by suction filtration, washed three times with cold water, and air dried to give 33.7 g (91%) of *m*-dinitrobenzene-^{14}C, mp 87–89 °C (lit.[11] mp 89.0–89.5 °C).

B. *m*-Nitroaniline-^{14}C. To a solution of 33.7 g (0.201 mol) of *m*-dinitrobenzene-^{14}C in 600 ml of ethanol was added 300 ml of 20% ammonium sulfide solution. The mixture was stirred at reflux for 2 h, cooled to room temperature, and then poured into 1500 ml of cold water. The precipitate was collected by suction filtration. The mother liquor was extracted four times with ether. The combined ether solutions were dried over anhydrous magnesium sulfate and then evaporated to dryness. This residue and the precipitate were combined and crystallized from water to give 16.5 g (60%) of *m*-nitroaniline-^{14}C, mp 110–111 °C (lit.[12] mp 112.5 °C).

C. *m*-Chloronitrobenzene-^{14}C. *m*-Nitroaniline-^{14}C (16.5 g, 0.120 mol) was dissolved in a hot solution of 48 ml of concentrated hydrochloric acid in 30 ml of water, and the resulting liquid was cooled to 0 °C in an ice–salt bath. A solution of 9.12 g (0.132 mol) of sodium nitrite in 30 ml of water was added dropwise with continuous stirring and cooling. The cold solution was filtered and then added slowly to a solution of 15.0 g (0.152 mol) of cuprous chloride in 45 ml of concentrated hydrochloric acid while keeping the temperature at 25–30 °C. The resulting mixture was refluxed for 10 min and then steam distilled until about 3 l. of distillate had been collected. The distillate was extracted with ether and the combined ether solutions were washed once with water, dried over anhydrous potassium carbonate, and then evaporated to dryness to give 13.7 g (80%) of yellowish solid, mp 46–48 °C (lit.[13] mp 46 °C).

D. *m*-Chloroaniline-^{14}C. A warm solution of 13.7 g (0.0874 mol) of *m*-chloronitrobenzene-^{14}C in 20 ml of glacial acetic acid was added slowly to a refluxing solution of 68.8 g (0.305 mol) of stannous chloride dihydrate in 115 ml of concentrated hydrochloric acid and 165 ml of methanol. The resulting mixture was concentrated over a period of 1 h to approximately 130 ml and then cooled and stirred into a solution of 136.5 g of sodium hydroxide in 875 ml of ice–water. The mixture was then extracted twice with 150-ml portions of ether. The combined extracts were dried over anhydrous potassium carbonate and the ether distilled. Distillation of the residual oil gave 10.2 g (92%) of *m*-chloroaniline-^{14}C, bp 113–116 °C (19 mm) [lit.[14] bp 118.5 °C (21 mm)].

E. *m*-Chloro-*N*-nitro-*N*-methylaniline-^{14}C. This compound was obtained by a procedure described previously[15] and crystallized from petroleum ether (bp 35–60 °C) to give a 24.5% yield of colorless crystals, mp 48.5–49.2 °C.

Anal. Calcd for $C_7H_7N_2O_2Cl$: C, 45.05; H, 3.78; N, 15.01. Found: C, 45.29; H, 3.74; N, 14.99.

3-Chloro-2-nitroaniline. To a stirred mixture of 90 ml of concentrated sulfuric acid and 24 ml of fuming (30%) sulfuric acid was added 10.75 g (0.050 mol) of 3-chloro-2-nitrobenzoic acid. After several minutes and with intermittent cooling to keep the temperature below 40 °C, 8.15 g (0.125 mol) of sodium azide was added in small portions. The mixture was stirred at 46–48 °C for 3.5 h and then cooled and poured slowly over cracked ice. The resulting mixture was neutralized with 40% sodium hydroxide and the product collected by suction filtration. Crystallization from a mixed solvent of benzene and ligroin (bp 65–90 °C) gave 8.36 g (91%) of orange needles, mp 108–109 °C (lit.[16] mp 108–108.5 °C).

3-Chloro-4-nitroaniline. *m*-Chloroacetanilide was nitrated with concentrated nitric acid in a mixture of concentrated sulfuric acid and glacial acetic acid by the procedure of Mayes and Turner.[17] The desired 3-chloro-4-nitroacetanilide was separated from the 3-chloro-6-nitroacetanilide by dissolving the mixture (65.5 g, 0.305 mol) in 2300 ml of boiling benzene. The solution was allowed to cool whereupon 3-chloro-4-nitroacetanilide crystallized. The solid was collected by suction filtration and then recrystallized from aqueous ethanol to give 37.6 g (58%) of 3-chloro-4-nitroacetanilide, mp 144.5–145.0 °C (lit.[18] mp 145 °C). The acetanilide was then hydrolyzed by heating at 110 °C for 10 min with 150 g of concentrated sulfuric acid. The solution was cooled and poured slowly over ice. The solid was collected by suction filtration, washed once with water, and then crystallized from aqeuous ethanol. Two additional crystallizations from benzene gave 17.3 g (59%) of 3-chloro-4-nitroaniline, mp 161–162 ° (lit.[18] mp 158.4 °C).

3-Chloro-5-nitroaniline. A. 3,5-Dinitrochlorobenzene. A solution of 9.76 g (0.14 mol) of sodium nitrite in 32 ml of water was slowly stirred into an ice-cold solution of 22.0 g (0.12 mol) of 3,5-dinitroaniline in 55 ml of concentrated hydrochloric acid and 20 ml of water. The temperature was maintained at 0–5 °C by addition of ice. The resulting mixture was poured slowly and with intermittent cooling into 16 g of cuprous chloride dissolved in 48 ml of concentrated

Table II. Derivatives of *m*-Chloroaniline[f]

Ring substn[g]	Solvent[a]	%[b]	Mp, °C	Registry no.
		N-*p*-Toluenesulfonyl		
3-Cl	Et–HA	99	136.5–137.5[c]	19377-04-9
3-Cl-2-NO_2	Et–W	22	143.5–144.3	60498-60-4
3-Cl-4-NO_2	HA–W	73	120.5–121.5	60498-61-5
3-Cl-5-NO_2	Et–W	89	137.0–138.0	60498-62-6
		N-Methyl-*N*-*p*-toluenesulfonyl		
3-Cl	Pet.	97	78.0–78.5	35462-50-1
3-Cl-2-NO_2	Et–W	96	135.0–136.0	60498-63-7
3-Cl-4-NO_2	Me	85	99.0–100.0	60498-64-8
3-Cl-5-NO_2	Me	96	148.0–149.0	60498-65-9
		N-Methyl		
3-Cl		93	*d,e*	
3-Cl-2-NO_2	Pet.	87	65.5–66.5	
3-Cl-4-NO_2	HA	65	107.0–108.0	
3-Cl-5-NO_2	Et–W	92	117.0–118.0	

[a] Et = ethanol, Me = methanol, W = water, HA = acetic acid, Pet. = petroleum ether (bp 35–60 °C). [b] Percent yield. [c] Lit. mp 134 °C [F. E. King, T. J. King, and I. H. M. Muir, *J. Chem. Soc.*, 5 (1946)]. [d] Bp of 89–90 °C (1.8 mm) compares with lit. bp 235 °C [J. von Braun and O. Kruber, *Ber.*, **46**, 3470 (1913)]. [e] Mp of *N*-acetyl derivative of 91.5–92.5 °C compares with reported mp of 92.5 °C [W. Staedel, *Ber.*, **19**, 1947 (1886)]. [f] Satisfactory combustion analytical data for C, H, N (±0.4%) were provided for these compounds. Ed. [g] Registry no. are, respectively, 108-42-9, 59483-54-4, 825-41-2, 5344-44-5.

hydrochloric acid. The mixture was refluxed for 10 min and then steam distilled until approximately 5.5 l. of distillate had passed over. The product was collected by suction filtration. The filtrate was extracted with methylene chloride and the solution was dried over anhydrous potassium carbonate and evaporated. Crystallization of the combined fractions from ethanol gave 14.8 g (61%) of 3,5-dinitrochlorobenzene, mp 51–52 °C (lit.[19] mp 53 °C).

B. 3-Chloro-5-nitroaniline. A mixture of 14.7 g (0.0726 mol) of 3,5-dinitrochlorobenzene, 200 ml of ethanol, and 110 ml of 20% ammonium sulfide solution was refluxed with stirring for 1 h. After cooling to room temperature, the mixture was filtered. The filtrate was poured into 800 ml of cold water and the solid was filtered off. This filtrate was extracted three times with 200-ml portions of ether. The combined ether solutions were dried over anhydrous potassium carbonate and then evaporated to dryness. The residue was combined with the previous solid and extracted once with boiling water. The aqueous solution was cooled and gave 3.28 g (26%) of 3-chloro-5-nitroaniline, mp 132–133 °C (lit.[20] mp 133–134 °C).

Preparation of Substituted *N*-Methylanilines from Substituted Anilines. The substituted aniline was treated with *p*-toluenesulfonyl chloride in pyridine to convert to the *N*-*p*-toluenesulfonyl derivative. The latter was alkylated with methyl sulfate in an aqueous dioxane solution of sodium hydroxide. The toluenesulfonyl group was then removed from the amino group by heating the *N*-methyl-*N*-*p*-toluenesulfonyl compound with an acetic acid solution of sulfuric acid. The details of this procedure have been described.[8] The intermediates and products from this sequence of steps are listed in Table II.

5-Chloro-2-nitro-*N*-methylaniline. Into a heavy-walled glass tube were placed 3.84 g (0.02 mol) of 2,4-dichloronitrobenzene, 22 ml of ethanol, and 5.0 ml of 6.0 N methylamine solution. The tube was sealed and heated in a steam bath for 20.5 h. The contents were removed and filtered by suction. The product was washed with water and then crystallized from ethanol to give 2.04 g (55%) of amine, mp 104.5–105.5 °C. A second fraction, 0.22 g (6%), mp 88–90 °C, was also isolated. Repetition of this experiment with 7.68 g (0.04 mol) of 2,4-dichloronitrobenzene gave 4.89 g (65%) of the nitroaniline, mp 99–102 °C. All fractions were combined and recrystallized from ethanol to give 6.22 g of orange needles, mp 106–107 °C (lit.[21] mp 106–107 °C).

Isotope Dilution Analysis of Rearrangement Products of *m*-Chloro-*N*-nitro-*N*-methylaniline. A. Rearrangement. A solution of 933.0 mg (5.00 mmol) of *m*-chloro-*N*-nitro-*N*-methylaniline-^{14}C in 80.0 ml of dioxane in a 2000-ml volumetric flask was diluted very rapidly with sufficient aqueous perchloric acid–sodium perchlorate solution (0.501 M-$HClO_4$, 0.501 M $NaClO_4$), which had previously been thermostated at 55 °C, to bring the volume of the solution to the mark. The flask was shaken by inversion several times and placed in a constant temperature bath at 55.0 °C for 2 h. Then 5.00 g of sulfamic acid was added and heating continued for an additional 30 min. The mixture was then cooled rapidly to room temperature and the volume adjusted to the mark by the addition of dioxane. After the contents were mixed thoroughly, aliquots were removed and treated as described below.

Table III. Yields of Products from the Rearrangement of *m*-Chloro-*N*-nitro-*N*-methylaniline

Ring substn[a]	Mp,[b] °C	% yield sample 1[c]	% yield sample 2[d]	% yield average[e]
3-Cl	92.5–93.5[f]	13.0	13.7	13.4 ± 0.4
3-NO_2	64.6–66.0	0.0	0.0	0.0 ± 0.0
3-Cl-2-NO_2	67.0–67.5	18.5	17.7	18.1 ± 0.4
3-Cl-4-NO_2	107.2–107.8	34.7	34.8	34.8 ± 0.1
3-Cl-5-NO_2	117.1–117.9	0.0	0.0	0.0 ± 0.0
5-Cl-2-NO_2	106.5–107.2	30.9	32.2	31.6 ± 0.7

[a] Substitution in the ring of *N*-methylaniline. [b] Melting points of compounds analyzed, can be compared with similar data in previous parts of Experimental Section. [c] Sample recrystallized four times. [d] Sample recrystallized seven times. [e] Assays of samples 1 and 2 showed that they had constant activity and so they were averaged. [f] Melting point of *N*-acetyl derivative.

B. Dilution and Isolation of 3-Chloro-x-nitro-*N*-methylanilines and *m*-Nitro-*N*-methylaniline. An aliquot (300.0 or 350.0 ml) of the above reaction mixture was thoroughly mixed with an excess (2.50 or 5.00 mmol) of inactive 3-chloro-x-nitro-*N*-methylaniline or *m*-nitro-*N*-methylaniline dissolved in 50.0 ml of dioxane. The solution was made basic with 10% aqueous sodium hydroxide and then extracted with one 100-ml portion and three 50-ml portions of ether. After the combined ether solutions were dried over anhydrous magnesium sulfate, they were evaporated to dryness. The residue was dissolved in ether and chromatographed on an alumina column using ether as the eluent. The fraction containing the desired nitro compound was evaporated and the remaining solid was crystallized four times from a suitable solvent (see Table II). The activity of the product was determined and it was then recrystallized three more times and analyzed again.

C. Dilution and Isolation of a Derivative of *m*-Chloro-*N*-methylaniline. The dilution of the reaction product with *m*-chloro-*N*-methylaniline and the isolation of this substance was carried out as described in B above. The oil remaining after evaporation of the ether extracts was treated with 2.0 ml of acetic anhydride and 2 drops of concentrated sulfuric acid and heated on a steam bath for 5 min. After the addition of 15 ml of methanol, the mixture was again heated on the steam bath and evaporated to dryness under aspirator vacuum.

D. Determination of Activities. The substances to be analyzed for carbon-14 content were dried in a vacuum desiccator over potassium hydroxide and paraffin chips for at least 24 h. Their activities were determined by "burning" carefully weighed samples to carbon dioxide with Van Slyke–Folch solution,[22] collecting the carbon dioxide in an ionization chamber, and measuring four or five "rates of drift" by means of a Cary Model 31 vibrating reed electrometer. This procedure has been described in detail.[23]

E. Calculation of Percentages of Products. The following equation was used to calculate percentages from the averaged rates of drift for each compound.

$$\% = \frac{M_0 M' V_0 w (a - b)}{M V w_0 [S_0 w' - M' (a - b)]}$$

M = mol wt of reactant
M_0 = mol wt of product
M' = mol wt of assayed derivative of product
w_0 = mg of reactant reacted
w = mg of inactive diluent used
V_0 = ml of original reaction solution
V = ml of aliquot of reaction solution
a = rate of drift (mV/min) from CO_2 from w' mg.
b = rate of drift (mV/min) from inactive CO_2
S_0 = specific activity (mV min^{-1} $mmol^{-1}$) of reactant

The last quantity, S_0, is available from

$$S_0 = M_0(a_0 - b)/W'_0$$

W'_0 = mg of pure reactant combusted
a_0 = rate of drift (mV/min) from CO_2 from W'_0 mg.

The value of S_0 used in the computation of percentages was the average of four separate determinations. The results of these calculations are set forth in Table III.

Registry No.—**5,** 23042-41-3; **6,** 7006-52-2; **7,** 619-26-1; **8,** 60498-57-9; **9,** 60498-58-0; **10,** 60498-59-1; **11,** 35966-84-8.

References and Notes

(1) This investigation was supported in part by the National Science Foundation (Grants GP-1970 and GP-8996).
(2) To whom correspondence should be addressed.
(3) W. N. White, D. Lazdins, and H. S. White, *J. Am. Chem. Soc.*, **86,** 1517 (1964)
(4) W. N. White and J. T. Golden, *J. Org. Chem.*, **35,** 2759 (1970)
(5) D. V. Banthorpe and J. G. Winter, *J. Chem. Soc., Perkin Trans. 2,* 1259 (1972), and previous papers in this series.
(6) M. J. S. Dewar in "Molecular Rearrangements", Part 1, P. de Mayo, Ed., Interscience, New York, N.Y., 1963, pp 306–313.
(7) D. V. Banthorpe, *Chem. Rev.*, **70,** 295 (1970).
(8) W. N. White and J. T. Golden, *J. Org. Chem.*, **35,** 2759 (1970), and preceding papers in this series.
(9) W. N. White in "Mechanisms of Molecular Migrations", Vol. 3, B. S. Thyagarijan, Ed., Wiley, New York, N.Y., 1971, pp 109–143.
(10) W. N. White and C. D. Slater, *J. Org. Chem.*, **26,** 3631 (1961).
(11) J. H. William and C. H. Schwingel, *J. Am. Chem. Soc.*, **50,** 362 (1928).
(12) J. F. T. Berliner and O. E. May, *J. Am. Chem. Soc.*, **47,** 2351 (1925).
(13) S. Sugden and H. Wilkins, *J. Chem. Soc.*, **127,** 2517 (1925).
(14) N. V. Sidgwick and H. E. Rubie, *J. Chem. Soc.*, **119,** 1013 (1921).
(15) W. N. White, E. F. Wolfarth, J. R. Klink, J. Kindig, C. Hathaway, and D. Lazdins, *J. Org. Chem.*, **26,** 4124 (1961).
(16) L. K. Dyall and K. H. Pausacker, *Aust. J. Chem.*, **11,** 491 (1958).
(17) H. A. Mayes and E. E. Turner, *J. Chem. Soc.*, 692 (1928).
(18) A. F. H. Lobry de Bruyn, *Recl. Trav. Chim. Pays-Bas,* **36,** 126 (1916).
(19) R. Bader, *Ber.*, **24,** 1655 (1891).
(20) J. B. Cohen and D. McCandlish, *J. Chem. Soc.*, **87,** 1264 (1905).
(21) R. Stoermer, and P. Hoffman, *Ber.*, **31,** 2532 (1898).
(22) D. F. Van Slyke, J. Folch, and J. Plazin, *J. Biol. Chem.*, **136,** 509 (1940).
(23) O. K. Neville, *J. Am. Chem. Soc.*, **70,** 3501 (1948); V. F. Raaen and G. A. Ropp, *Anal. Chem.*, **25,** 174 (1953).

Synthesis and Chemistry of Some 2-Aminoethenesulfonyl Fluorides. An Unusual Manganese Dioxide Oxidation

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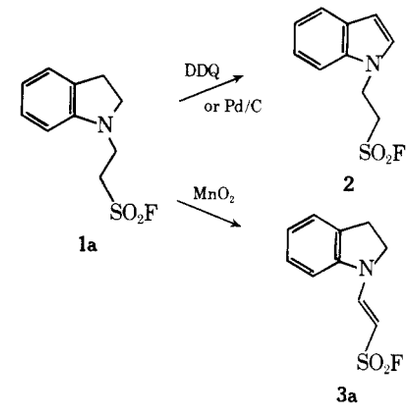
Some recent work in this laboratory demonstrated the facile fluorosulfonylethylation of various amines with vinylsulfonyl fluoride.[1] We wish to report that β-fluorosulfonylethylamines **1** are dehydrogenated by active manganese dioxide to afford novel 2-aminoethenesulfonyl fluorides.

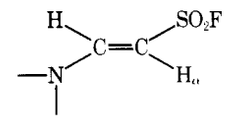
$$CH_2{=}CH{-}SO_2F + \begin{matrix}R_1\\R_2\end{matrix}\!\!>\!N{-}H \longrightarrow \begin{matrix}R_1\\R_2\end{matrix}\!\!>\!N{-}CH_2{-}CH_2{-}SO_2F$$

1

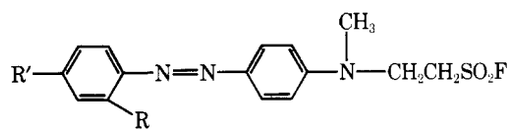
R = H, alkyl, or aryl

Jansen and co-workers have described the dehydrogenation of indolines with active manganese dioxide.[2] We found that, although indole **2** could be prepared from indoline **1a** by using dichlorodicyanobenzoquinone or palladium on carbon, reaction of **1a** with active MnO_2 afforded a new substance, **3a,** which was isomeric with **2.** Compound **3a** was assigned the enaminosulfonyl fluoride structure shown on the basis of its empirical formula and spectral properties (see Experimental Section). In particular, the ^1H NMR spectrum of **3a** points to the presence of a highly polarized olefinic system, wherein H_α is coupled with the fluorine atom.

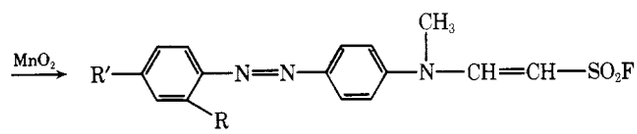




In view of the unusual course of this oxidation, the reaction of a series of substituted 2-aminoethanesulfonyl fluorides with MnO_2 was carried out; Table I gives the structures and yields. Two additional examples were provided by the preparation of dyes **3g** and **3h.** Further experiments delineated the scope



1g, R = SO_2CH_3; R' = NO_2
1h, R = H; R' = SO_2F



3g, R = SO_2CH_3; R' = NO_2 (56%)
3h, R = H; R' = SO_2F (59%)

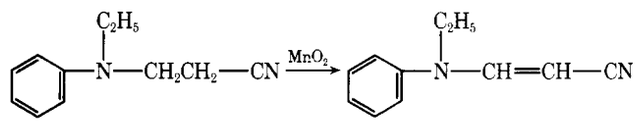
of the oxidation. Sulfonyl fluorides **4** and **5** did not react with MnO_2, and β-cyanoethylamine **6** was converted to enamine **7** very slowly and in poor yield.

$$CH_3(CH_2)_2CH_2SO_2F \xrightarrow{MnO_2} \text{no reaction}$$

4

$$ClCH_2CH_2SO_2F \xrightarrow{MnO_2} \text{no reaction}$$

5



6 **7** (22%)

Henbest and co-workers[3,4] have reported the isolation of low yields of enamines as intermediates in the MnO_2 dealkylation of tertiary amines; the enamines were generally unstable in the presence of MnO_2. In the case at hand, the stability of enaminosulfonyl fluorides (vide infra) could account for the good yields obtained. One possible mechanism for the oxidation involves the following electron-transfer process. That electron transfer from β-fluorosulfonylethylamines does indeed lead to the observed products was demonstrated by uv irradiation of **1b** in the presence of benzophenone; **3b** was