The Acid-Catalyzed Nitramine Rearrangement. IV. The Influence of Aromatic Ring Substituents on Rearrangement Rate[1-3]

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The rates of rearrangement of 16 *meta*- and *para*-substituted N-nitro-N-methylanilines were determined and correlated by means of Hammett's equation. The best fit of the experimental data was obtained when the results were plotted against σ^+ constants ($\rho = -3.7$). The π-complex and cartwheel mechanisms of the nitramine rearrangement are incompatible with these findings. The experimental observations can be interpreted by a mechanism in which the rate-determining step is the homolytic scission of the nitrogen–nitrogen bond in the protonated nitramine.

Previous investigations in this series[1] have demonstrated that the acid-catalyzed aromatic nitramine rearrangement involves reversible protonation of the substrate followed by a rate-determining unimolecular reaction of the protonated nitramine. Product studies[1] suggest that the latter process may be a cleavage of the N–N bond in the nitramine to yield a pair of solvent-caged radicals, which may either recombine to yield isomerized products or may dissociate, be reduced, and form nitrous acid and aromatic amine. Further information about the rate-determining step should be
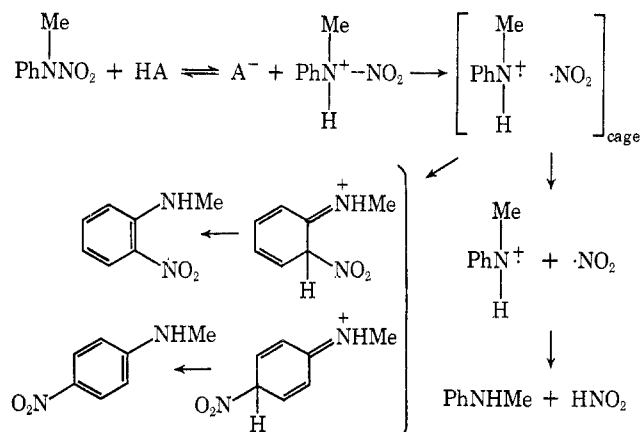
available from a study of the influence of aromatic ring substituents on the rate of the nitramine rearrangement. Since the reaction is subject to specific acid catalysis, substituent effects must reflect not only the electronic requirements of the protonation step, but also those of the N–N bond-breaking step.
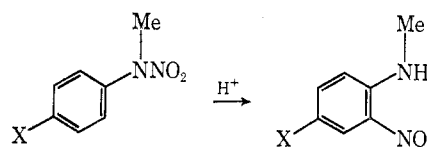
The effect of structure on the rate of the nitramine rearrangement was implicit in the results of some kinetic studies carried out in the early 1900's.[4] The reaction of 2,4-dichloro-N-nitroaniline was 10 times slower than the isomerization of N-nitroaniline and 25 times slower than the rearrangement of 2-bromo-4-methyl-N-nitroaniline, implying that electron-withdrawing groups retard the reaction. Similar effects are apparent in the comparative behavior of 4,N-dinitro-N-methylaniline

and 2,4,N-trinitro-N-methylaniline.[5] The former compound, being less encumbered with electron-attracting substituents, rearranges more easily.

These fragmentary results are, however, far from being definitive, and much more precise information about the nature of the N–N bond cleavage should be obtainable from a systematic study of the influence of aromatic ring substituents on the rate of rearrangement.

Results and Discussion

Products of Rearrangement of Substituted Nitramines.—Previous investigations in this series[1] have shown that the nitro group migrates only to the *ortho* and *para* positions of the aromatic ring and that a small fraction of the product corresponds to complete loss of the nitro group. This study was more superficial than the previous ones in that only the major products of rearrangement were identified and accounted for. However, the results summarized in Tables I and II confirm the previous findings. Thus the principal product formed upon rearrangement of a nitramine substituted in the *para* position with an electron-releasing substituent (MeO, MeS, Me, F, Cl, Br, Ph, and PhO) is the *ortho* nitroaniline (formed in 55–85% yields in the cases studied). The presence of strongly electron-

withdrawing substituents (NC, O_2N, and $MeSO_2$) in the *para* position causes the yield of the *ortho* nitro compound to drop to 25–45%. The nitrated product from *p*-bromo-N-nitro-N-methylaniline contained 10–17% *p*-nitro-N-methylaniline from bromine atom displacement. A similar displacement occurred in the *p*-chloro compound only to the extent of 0.2%.

Substituent Effects on Rearrangement Rates.—The second-order rate constants for the acid-catalyzed isomerization of 16 *meta*- and *para*-substituted N-nitro-N-methylanilines were determined and are listed in Table III. These rate constants cover a range of over a half-millionfold. Electron-donating groups increase the rate and electron-withdrawing groups slow the reaction indicating that the forward course of the

(1) Previous papers in this series: W. N. White, D. Lazdins, and H. S. White, *J. Amer. Chem. Soc.*, **86**, 1517 (1964); W. N. White, C. Hathaway, and D. Huston, *J. Org. Chem.*, **35**, 737 (1970).

(2) Part of this work has been reported in preliminary form: W. N. White, J. R. Klink, D. Lazdins, C. Hathaway, J. T. Golden, and H. S. White, *J. Amer. Chem. Soc.*, **83**, 2024 (1961).

(3) This work was supported by Grants G-7345 and GP-1970 from the National Science Foundation.

(4) K. J. P. Orton, *Brit. Assoc. Advan. Sci. Rep.*, 115 (1908); A. E. Bradfield and K. J. P. Orton, *J. Chem. Soc.*, 915 (1929).

(5) E. D. Hughes and G. T. Jones, *ibid.*, 2678 (1950).
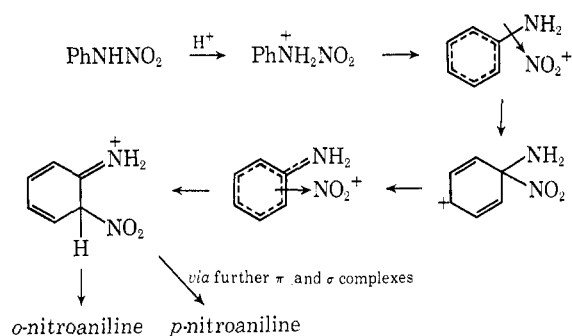
TABLE I
2-NITRO-4-X-N-METHYLANILINES

X	Registry no.	Yield, %	Solvent^a	Mp, °C	Lit. mp, °C
MeS	23042-45-7	63	MeOH–H$_2$O	64–65	...^{b}
MeO		85	MeOH	98–99	97–98^c
Me		80	MeOH	84.5–85	84–85^d
F	704-05-2	69	MeOH	74.1–74.6	...^{e}
Cl		55	EtOH	107–108	109–110^f
Br		62	MeOH	101.9–102.4	101–102^g
Ph		85	EtOH	113–114	112^h
PhO	23042-47-9	55	Pet. ether	104–105	...^{i}
PhCO		60	PhH–MeOH	210–211	200^j
NC		36	PhH	168.5–169.3	169^k
MeSO$_2$		25	PhH–MeOH	193.4–193.9	193.5^l
O$_2$N		35	PhH	179–180	176–177^f

^{a} Pet. ether = petroleum ether (bp 65–90°). ^{b} *Anal.* Calcd for C$_8$H$_{10}$N$_2$O$_2$S: C, 48.47; H, 5.08; N, 14.13. Found: C, 48.46; H, 5.20; N, 14.20. ^{c} A. M. Simonov and P. A. Uglov, *Zh. Obshch. Khim.*, 21, 884 (1951). ^{d} L. Gatterman, *Chem. Ber.*, 18, 1487 (1885). ^{e} *Anal.* Calcd for C$_7$H$_7$FN$_2$O$_2$: C, 49.41; H, 4.15; N, 16.47. Found: C, 49.00, 49.41; H, 4.18, 4.21; N, 16.33. ^{f} R. Stoermer and P. Hoffmann, *Chem. Ber.*, 31, 2523 (1898). ^{g} J. J. Blanksma, *Rec. Trav. Chim. Pays-Bas*, 21, 272 (1902). ^{h} F. Bell and P. H. Robinson, *J. Chem. Soc.*, 1127 (1927). ^{i} *Anal.* Calcd for C$_{13}$H$_{12}$N$_2$O$_3$: C, 63.93; H, 4.95; N, 11.48. Found: C, 63.74; H, 5.05; N, 11.50. ^{j} J. van Alphen, *Rec. Trav. Chim. Pays-Bas*, 49, 383 (1930). ^{k} J. F. Mattaar, *ibid.*, 41, 24 (1922). ^{l} E. Scoffone, P. de la Llosa, and M. Justisz, *Bull. Soc. Chim. Fr.*, 1553 (1959).

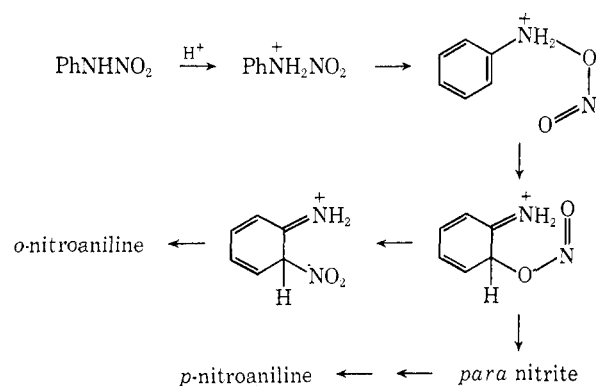rearrangement involves electron depletion at the reaction center.

These kinetic results were treated by means of the Hammett equation. The best fit of the experimental data was afforded by σ^+ constants (correlation coefficient = 0.99). The straight-line plot had a slope ρ of −3.7. The correlation coefficients obtained with σ and σ^- constants were less than 0.92 (representative of a poor to fair fit[6]) and the points deviated considerably from a straight line. The σ^+ constants are defined by reactions[7] in which an electron deficiency is generated at the reaction center in such a way that it can be delocalized to the aromatic ring by resonance. The requirement of σ^+ constants for correlation of the nitramine rearrangement suggests that the series of steps leading from the unprotonated nitramine to the rate-limiting transition state must also involve creation of an electron deficiency delocalizable to the aromatic nucleus. The negative reaction constant, ρ, substantiates the conclusion that the substrate becomes more electron deficient as the highest energy transition state is approached. The magnitude of ρ indicates that there must be strong interaction between the reaction center and the substituent.

These findings are not compatible with the "π-complex" mechanism[8] nor the "cartwheel" mechanism[9] for the nitramine rearrangement. In the π-complex mechanism it is proposed that the protonated nitramine is transformed through a series of alternate σ and π complexes into the final products. A reaction proceeding by this path would probably be correlated by σ or σ^- constants and a small value of ρ. The amino-group electrons in the nitramine are not readily available for conjugation with the aromatic ring, since they will be largely delocalized to the highly electron-attracting nitro group. When the nitrogen–nitrogen bond is broken in the transition state for π-complex formation, these electrons should be freed for resonance with the

(6) H. H. Jaffe, *Chem. Rev.*, 53, 191 (1953).

(7) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963.

(8) M. J. S. Dewar in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc , New York, N. Y., 1963, pp 306–313.

(9) S. Brownstein, C. A. Bunton, and E. D. Hughes, *J. Chem. Soc.*, 4354 (1958).

o-nitroaniline   *p*-nitroaniline

ring. If the process were this simple, a positive ρ and σ^- constants would be required. However, the liberated nitronium ion will probably interact with the π cloud of the aromatic system and reduce its electron richness somewhat.

In the cartwheel mechanism, it is supposed that the protonated nitramine isomerizes to a *nitritoamine*, which then undergoes a Claisen-like rearrangement to an *ortho* nitrite. A *para* nitrite can arise from the latter by a similar migration. Isomerization of the nitrites leads to C-nitro intermediates like those formed in direct nitration reactions. Proton loss from these species yields the *o*- and *p*-nitroanilines. The effect of sub-

p-nitroaniline ⟵ ⟵ *para* nitrite

stituents on this overall process is more difficult to predict. Only the protonation step involves a large polarity change, and this should be correlated by σ or σ^- constants and a small negative ρ (−1 to −2). In

TABLE II

RATES OF REARRANGEMENT AND PRODUCT YIELDS FOR m- AND p-X-N-NITRO-N-METHYLANILINES

X	Temp, °C[a]	Concn, M	Concn, HClO4[b]	No. of runs	$10^4 k_2$, M^{-1} sec^{-1}	2-NO2,[c] %	p-NO2,[d] %
p-MeO	30.00	0.00200	0.00100	5	11800 ± 200	68 ± 2	
	15.00	0.00200	0.00100	4	2450 ± 100	69 ± 1	
	0.17	0.0200	0.0100	6	452 ± 3	68 ± 2	
p-MeS	30.00	0.00200	0.00100	4	7450 ± 110		
	15.00	0.00200	0.00100	4	1750 ± 60		
	0.17	0.0200	0.0100	4	345 ± 4		
p-Me	55.00	0.0100	0.00501	4	3660 ± 80	82 ± 1	
	40.00	0.0200	0.00100	6	820 ± 18	82 ± 4	
	25.00	0.0200	0.00100	4	139 ± 3	84 ± 1	
H	55.00	0.0200	0.0100	6	266 ± 6	46 ± 2	28 ± 2
	40.00	0.0200	0.0100	6	34.8 ± 0.8	48 ± 0	28 ± 1
	25.00	0.0802	0.0401	4	4.77 ± 0.04	52 ± 0	28 ± 0
p-F	55.00	0.0200	0.0100	6	233 ± 3	60 ± 1	0
	40.00	0.1002	0.0501	4	41.0 ± 0.5	62 ± 1	0
	25.00	0.0401	0.0200	4	6.47 ± 0.04	61 ± 1	0
p-Cl	55.00	0.1002	0.0501	9	157 ± 6	84 ± 2	0.2 ± 0.1
	40.00	0.1002	0.0501	4	28.4 ± 0.4	80 ± 4	0.2 ± 0.1
	25.00	0.1002	0.0501	4	4.47 ± 0.10		
p-Br	55.00	0.1002	0.0501	4	128 ± 4	67 ± 1	9.4 ± 0.3
	40.00	0.1002	0.0501	4	25.9 ± 0.8	62 ± 2	12.1 ± 0.4
	25.00	0.1002	0.0501	4	3.81 ± 0.09	56 ± 1	16.7 ± 0.1
p-CN	70.00	1.002	0.501	5	12.2 ± 0.4	43 ± 3	
	55.00	1.002	0.501	6	1.93 ± 0.05	46 ± 2	
	40.00	1.002	0.501	4	0.292 ± 0.007	46 ± 2	
p-MeSO2	85.00	0.501	0.251	4	18.7 ± 0.3	32 ± 1	
	70.00	0.501	0.251	6	3.04 ± 0.17	31 ± 1	
	55.00	1.002	0.501	4	0.452 ± 0.006	37 ± 1	
p-NO2	80.00	1.002	0.501	5	10.1 ± 0.1	41 ± 1	1.0 ± 0.1
	65.00	1.002	0.501	8	2.05 ± 0.06	41 ± 1	2.0 ± 0.1
	55.00	1.002	0.501	4	0.542 ± 0.009	40 ± 3	0.5 ± 0.5
m-MeO	55.00	0.0401	0.0200	4	458 ± 15		
	40.00	0.200	0.1002	4	82.8 ± 1.2		
	25.00	1.002	0.501	5	14.7 ± 0.8		
m-PhO	55.00	0.1002	0.0401	4	148 ± 8		
	40.00	0.501	0.200	6	23.9 ± 0.3		
	25.00	1.002	0.501	4	3.32 ± 0.10		
m-Me	55.00	0.0401	0.0200	4	672 ± 25		
	40.00	0.1002	0.0401	5	120 ± 6		
	25.00	1.002	0.501	4	18.3 ± 0.4		
m-F	70.00	0.1002	0.0401	4	143 ± 4		
	55.00	0.501	0.200	4	26.1 ± 0.3		
	40.00	1.002	0.501	4	4.58 ± 0.16		
m-Cl	70.00	0.1002	0.0401	4	103 ± 2		
	55.00	1.002	0.501	8	18.7 ± 0.8		
	40.00	1.002	0.501	8	2.92 ± 0.05		
m-Br	70.00	0.1002	0.0401	4	100 ± 2		
	55.00	1.002	0.501	5	18.2 ± 0.4		
	40.00	1.002	0.501	6	2.82 ± 0.06		

[a] Temperature of reaction, ±0.02°. [b] Ionic strength maintained constant at 1.002 M by addition of NaClO4. [c] Per cent of 2-nitro-4-X-N-methylaniline formed. [d] Per cent of p-nitro-N-methylaniline formed.

TABLE III

RATE CONSTANTS FOR REARRANGEMENT OF m- AND p-X-N-NITRO-N-METHYLANILINE[a]

| X	$10^6 k_2$, mol^{-1} sec^{-1}	X	$10^6 k_2$, mol^{-1} sec^{-1}
p-MeO	3,060,000[b]	p-Br	2590
p-MeS	1,840,000[b]	m-PhO	2390
p-Me	82,000	m-F	458
m-Me	12,000	m-Cl	290
m-MeO	8,280	m-Br	282
p-F	4,100	p-CN	29,2
H	3,480	p-NO2	8.05[b]
p-Cl	2,840	p-MeSO2	5.40[b]

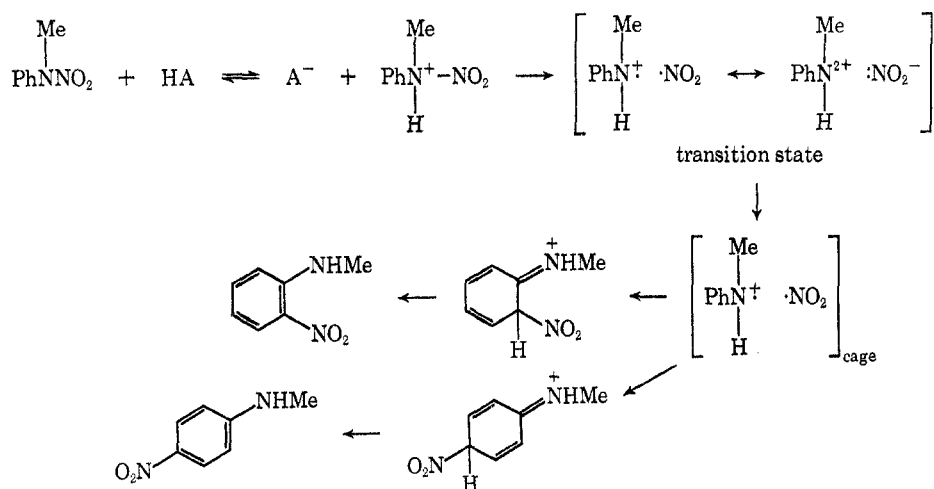[a] T = 40.00 ± 0.02°. [b] Extrapolated from other temperatures.

the nitramine–nitritoamine isomerization, a less electronegative center becomes attached to the amino nitrogen, and thus this process should require σ constants and a positive ρ. The *ortho* nitrite formed by rearrangement has considerable electron deficiency centered at the two positions *meta* to the amino group but not *para* to it. The substituent–rate data indicate that a sizable electron deficiency, which is delocalized to the *para* (but not the *meta*) position of the aromatic ring, is developed at the reaction center. The C-nitrite–C-nitro isomerization should be effected by substituents in the reverse manner of their influence on the N-nitro–N-nitrite change. Proton loss from the final intermediates is not kinetically significant, and thus need

not be considered in the prediction or interpretation of substituent effects. Regardless of what is chosen as the rate-determining step in the cartwheel mechanism, it is impossible to interpret the observed rate effects of substituents in terms of their influence on this and the preceding steps.

However, a mechanism involving cleavage of the nitrogen–nitrogen bond in the protonated nitramine could lead to the observed results. This would be true if this bond broke symmetrically to yield a pair of radicals in a solvent cage or if it broke unsymmetrically, both bond electrons becoming associated with the nitro group so that the amino nitrogen would be doubly electron deficient. Homolytic cleavage would produce an aromatic aminium cation radical. The electron
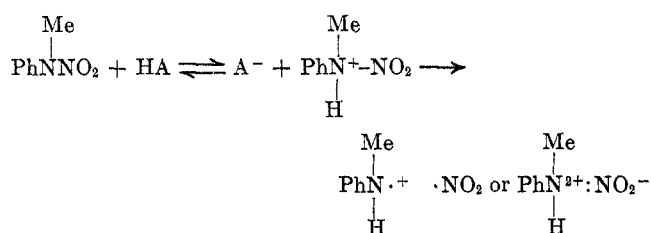
deficiency associated with the nitrogen atom in this species could be delocalized to the aromatic ring. Thus it would be expected that correlation of substituent effects on such a process would involve σ^+ constants and a large negative value of ρ. This supposition is supported by a number of studies that demonstrate that the generation of aromatic aminium cation radicals is correlated best by σ^+ constants. Polarographic oxidation of primary aromatic amines[10] requires σ^+ constants

hydroxyl group of phenols and from the α carbons of α-substituted toluenes have been found to give better linear plots with σ^+ than with σ constants.[14] All of these reactions involve generation of a radical center adjacent to an aromatic ring. Most processes of this type are correlated by σ^+ constants and a negative ρ. Thus the substituent-rate data for the nitramine rearrangement should exhibit a similar dependence on σ^+ constants if this process involves homolytic nitrogen–nitrogen bond breaking in the protonated nitramine.

Unsymmetrical cleavage of this nitrogen–nitrogen bond so that both electrons became associated with the departing nitro group would produce a highly electron-deficient, dipositive amino nitrogen. Substituents would have a very large effect on such a process. Correlation would require σ^+ constants and a large negative value of ρ. Reactions in which a single positive charge is developed on the less electronegative α carbon in substituted toluenes have ρ values of -2.3 to -4.7[7]. The observed reaction constant for the nitramine rearrangement (-3.7) is not large enough for a mechanism in which the nitrogen–nitrogen bond breaks to form an anilinium dication.

Thus it is likely that the protonated nitramine undergoes bond cleavage to form an anilinium cation radical and nitrogen dioxide. The transition state for this process is undoubtedly a resonance hybrid and partakes of the character of both modes of nitrogen–nitrogen bond scission described above. The magnitude of the substituent effect suggests that the least ionic structure makes the largest contribution. The mechanism most compatible with the results of this study is the following.

transition state

and large negative values of ρ (-4.3[10a] and -6.8[10b]) for fitting the effect of substituents. Oxidation of substituted anilines with N,N-diphenyl-N-picrylhydrazyl[11] is correlated by σ^+ constants and a ρ of -1.5. Methyl proton and nitrogen hyperfine splitting constants for substituted N,N-dimethylanilinium cation radicals[12] are linearly related to σ^+ constants. Thermolyses of t-butyl N-arylperoxycarbamates yield arylamine radicals[13] and are correlated by σ^+ constants ($\rho = -2.2$). Hydrogen atom abstraction from the

Experimental Section

Preparation of *m*- and *p*-X-N-Nitro-N-methylaniline.—The substituted N-nitro-N-methylanilines were obtained from the corresponding substituted anilines. Those aromatic amines bearing substituents that do not react with phenyllithium were subjected to alkaline nitration and the resulting nitramines were methylated with methyl sulfate to prepare[15] the title compounds. Anilines substituted with nitro, cyano, keto, and sulfonyl groups were converted into the corresponding diazonium salt and the latter was oxidized to the nitramine,[16] which was methylated.[17] The resulting *m*- and *p*-X-N-nitro-N-methylanilines were purified

(10) (a) R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, **81**, 5343 (1959); (b) J. Bacon and R. N. Adams, *ibid.*, **90**, 6596 (1968).

(11) J. C. McGowan, T. Powell, and R. Raw, *J. Chem. Soc.*, 3103 (1959).

(12) B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 5172 (1967).

(13) E. L. O'Brien, F. M. Beringer, and R. B. Mesrobian, *ibid.*, **81**, 1506 (1959).

(14) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963); G. A. Russell and R. C. Williamson, *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

(15) W. N. White, E. F. Wolfarth, J. R. Klink, J. Kindig, C. Hathaway, and D. Lazdins, *J. Org. Chem.*, **26**, 4124 (1961).

(16) E. Bamberger and K. Landsteiner, *Chem. Ber.*, **26**, 485 (1893).

(17) H. J. Backer, *Rec. Trav. Chim. Pays-Bas*, **31**, 142 (1912).

TABLE IV
m- AND *p*-X-N-NITRO-N-METHYLANILINES

X	Registry no.	Solvent	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
H	7119-93-9	a	36.6–37.6[b]	...	...	...	...	...	...
p-MeS	23042-28-6	c	71.0–72.0	48.47	5.08	14.13	48.65	5.19	14.07
p-MeO	22809-78-5	a	68.1–69.1	52.74	5.53	15.38	52.57	5.77	15.53
p-Me	23042-30-0	d	73.6–74.6[e]	...	...	...	...	...	...
p-F	655-56-1	a	68.6–69.1	49.41	4.15	16.47	49.18	4.26	16.50
p-Cl	23042-32-2	a	51.9–52.4[f]	...	...	...	...	...	...
p-Br	23042-33-3	d	84.0–84.9[g]	...	...	...	...	...	...
p-Ph	23042-34-4	h	137.8–138.5	68.40	5.30	12.28	68.60	5.32	12.23
p-PhO	23042-35-5	c	107.5–108.0	63.93	4.95	11.48	64.17	5.18	11.44
p-PhCO	23042-36-6	c	136.7–137.3	65.59	4.72	10.93	65.98	4.53	11.15
p-NC	23042-37-7	h	104.1–104.6	54.23	3.99	23.72	54.16	4.17	23.53
p-MeSO₂	23042-38-8	h	158–159	41.77	4.38	12.17	41.86	4.39	12.20
p-O₂N	16698-03-6	i	138.2–139.5[j]	...	...	...	...	...	...
m-Me	23042-40-2	k	...[k]	57.83	6.02	16.87	57.71	6.30	17.04
m-F	23102-81-0	a	24–25	49.41	4.15	16.47	49.31	4.28	16.50
m-Cl	23042-41-3	a	48.5–49.2	45.05	3.78	15.01	45.29	3.74	14.99
m-Br	23042-42-4	a	43.2–43.8	36.38	3.05	12.12	36.43	3.29	12.10
m-PhO	23042-43-5	a	44.0–44.5	63.93	4.95	11.48	64.14	4.87	11.39
m-MeO	23042-44-6	...[k]	...[k]	52.74	5.53	15.38	52.90	5.31	14.62

a Petroleum ether (bp 35–60°). *b* Literature mp 38.5–39.5°: E. Bamberger, *Chem. Ber.*, **27**, 359 (1894). *c* Cyclohexane. *d* Petroleum ether (bp 65–90°). *e* Literature mp 74.5–75.5°: J. Pinnow, *Chem. Ber.*, **30**, 833 (1897). *f* Literature mp 48–49°: E. Bamberger, *ibid.*, **30**, 1248 (1897). *g* Literature mp 83.5–84.5°: reference in *f*. *h* Benzene–cyclohexane. *i* Benzene. *j* Literature mp 140°: reference in *f*. *k* Liquid.

by chromatography on neutral alumina using ether as an eluent and then by crystallization from a suitable solvent. The appropriate data regarding these compounds are summarized in Table IV.

Isolation of Rearrangement Products of *p*-X-N-Nitro-N-methylaniline.—A solution of 1.00 g of the *p*-X-N-nitro-N-methylaniline in 50 ml of methanol and 50 ml of concentrated hydrochloric acid was refluxed for 2 hr and then allowed to stand for 20 hr at 25°. The solution was cooled to 0° and the solid product was collected by suction filtration. It was purified by chromatography on neutral alumina using benzene as eluent and by crystallization. Physical constants and crude-yield data are recorded in Table I.

Kinetic Measurements.—An aliquot of 1.022 *M* perchloric acid was pipeted into a 50-ml volumetric flask and diluted with 1.022 *M* sodium perchlorate solution to within 1 cm of the mark. After the flask had stood in a constant-temperature bath for 40 min, the volume was adjusted to the mark with 1.022 *M* sodium perchlorate solution. A 1.00-ml aliquot of a nitramine solution of accurately known concentration (*ca.* 10^{-2} *M*) in dioxane was added, the contents of the flask were mixed immediately, and the flask was returned to the thermostatic bath at once. Measured samples were withdrawn at appropriate intervals and quickly quenched by rapid addition to a volume of saturated lithium acetate solution sufficient to neutralize the acid. The absorbances of the quenched samples were determined at the wavelength of maximum extinction in the visible region. The optical density at "infinite" time was approximated from a reaction sample taken after 10 half-lives.

Pseudo-first-order rate constants were calculated from the experimental data in the usual way and these were converted into second-order constants by dividing by the constant concentration of acid, which was in large excess. The kinetics of rearrangement of each nitramine were studied at three different temperatures. Two different acid concentrations were used for each temperature, and at least two runs were made with each compound at a single

acid concentration and temperature. The results of these kinetic investigations are summarized in Table II.

Spectrophotometric Determination of Yields of 2-Nitro-4-X-N-methylanilines from Rearrangement of *p*-X-N-Nitro-N-methylanilines.—After completion of the kinetic runs described above, a 5.00-ml aliquot of the cooled reaction mixture was transferred to a 10.0-ml volumetric flask and 1.00 ml of 20% ammonium sulfamate was added. The resulting solution was heated at 100° for 30 min to destroy nitrous acid and remove N-nitroso groups. After cooling, the volume of liquid in the flask was brought to 10.0 ml by addition of acetic acid (8.8 *M*)-sodium acetate (1.1 *M*) buffer. The absorbance of the resulting solution was determined at five different wavelengths near the visible absorption maximum of the 2-nitro-4-X-N-methylaniline being determined.

Solutions of the pure 2-nitro-4-X-N-methylanilines in dioxane were treated in the same way as described above for solutions of the corresponding *p*-X-N-nitro-N-methylanilines in order to obtain extinction coefficients for the rearrangement products.

The concentration of 2-nitro-4-X-N-methylaniline in the reaction mixtures was calculated using Beer's law. Since the absorbance was determined at five wavelengths, there were five equations in one unknown (the concentration). The method of least squares was applied to these equations to obtain the best value.

Four of the nitramines produced two colored products on rearrangement—varying amounts of *p*-nitro-N-methylaniline were formed in the rearrangements of unsubstituted, *p*-chloro-, *p*-bromo-, and *p*-nitro-N-nitro-N-methylaniline in addition to the expected 2-nitro compound. The concentration of each colored substance was obtained by using the equation $A = abc + a'b'c'$, which has two unknown concentrations. Application of the method of least squares to the absorbances measured a five different wavelengths for each sample gave the best values for the concentrations of each of the products.

The results of this analysis are shown in Table II.