Anal. Calcd. for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.08; mol. wt., 214 (monomer), 428 (dimer), 642 (trimer), and 856 (tetramer). Found: C, 73.03; H, 6.75; N, 13.11. mol. wt., 640 (cryoscopic, camphor), 600 (cryoscopic, bromoform).

Intense infrared absorption (KBr disk) occurred at 3350, 1635, 1570, 1460, 1435, 1350, 1320, 1200, and 1170 cm.$^{-1}$.

The compound had an ultraviolet absorption maximum at 305 mμ in ethanol (ϵ 6.1×10^3).

B.—The compound (0.685 g.) with 2 g. of Raney nickel W-2 catalyst in 200 ml. of dioxane was hydrogenated at 1500 lb. in.$^{-2}$ for 5 hr. The catalyst was removed by filtration, and the solvent was removed under reduced pressure. A light brown solid (0.357 g., 51%) remained which was recrystallized from dioxane to give white crystals, m.p. 261–262° dec. This substance was identical (mixture melting point and infrared spectrum) with that obtained in the low pressure hydrogenation in ethyl acetate.

C.—Hydrogenation of the compound (0.4 g.) with 0.09 g. of platinum oxide catalyst in 75 ml. of chloroform at atmospheric pressure for 4 hr. gave a white solid, m.p. 248–249° dec., which was identified as 1-benzyl-3-carbamoylpiperidine hydrochloride by a mixture melting point (249–250°) and comparison of its infrared spectrum with that of an authentic sample.

D.—Hydrogenation of the compound (0.30 g.) with 0.10 g. of platinum oxide catalyst in 25 ml. of acetic acid at atmospheric pressure for 1.5 hr. gave 1-benzyl-3-carbamoylpiperidine, m.p. 124–125.5° (lit.[36] m.p. 123°). It was identified as a picrate, m.p. 218–221.5°, and by a mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

N-Nitrobenzamides. I. Synthesis, Spectra, and Structure[1]

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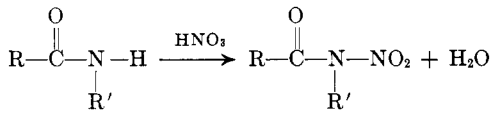
A series of monosubstituted N-nitro-N-methylbenzamides has been prepared by controlled direct nitration. Infrared and ultraviolet spectra are reported and discussed. Hydrolysis of the N-nitro-N-methylbenzamides yielded benzoic acids. The nitrobenzamides were converted readily to benzamides by reductive cleavage. Various similar nitration conditions applied to benzamide failed to yield N-nitrobenzamide, except as an unstable intermediate.

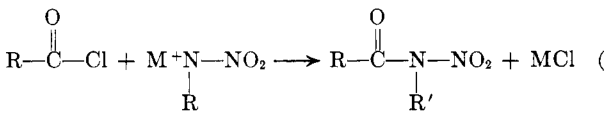
Two general synthetic methods can be expected to yield N-nitroamides: direct substitution of the nitro group on the amide nitrogen atom (equation 1) or



$$R-\overset{O}{\overset{\|}{C}}-\underset{R'}{\underset{|}{N}}-H \xrightarrow{HNO_3} R-\overset{O}{\overset{\|}{C}}-\underset{R'}{\underset{|}{N}}-NO_2 + H_2O \qquad (1)$$

I

acylation of the nitramine by the action of an acid halide upon the metal salt of the nitramine (equation 2).



$$R-\overset{O}{\overset{\|}{C}}-Cl + M^+\underset{R}{\underset{|}{N}}-NO_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-\underset{R'}{\underset{|}{N}}-NO_2 + MCl \qquad (2)$$

Due to the thermal instability of the N-nitroamides[2] the reaction conditions for either of these methods must be necessarily mild. Acylation of nitramines has been reported employing the silver salt of the nitramine. Either N- or O-acylation can occur. The evidence for the latter is indirect, and the O-acyl product is thermally unstable, preventing isolation and characterization.[2,3] The N-acyl product is formed in small yields,[3] and is stable at room temperature, permitting isolation in most cases. O-Alkylation is reported[4] to occur in the reaction of silver nitramide with alkyl iodides.

The direct nitration of amides has been effective if R′ is aliphatic, usually methyl, and R is aliphatic,[2] amino,[5,6] or alkoxyl.[2,7-9] If R is aromatic, substitution usually occurs on the benzene nucleus, with[10-13] or without[2,11,13] substitution on nitrogen. Three cases of exclusive N-nitration are found in which the benzene ring is strongly deactivated. Thus, two nitro groups[2] or three halogen atoms[13] were sufficiently deactivating to preclude nitration on the benzene ring. Thus, N-methyl-3,5-dinitrobenzamide[2] undergoes nitration at the amide function with 100% nitric acid and sulfur trioxide and only incomplete nitration with acetyl nitrate reagents. Nitration of the amide function occurred when concentrated nitric acid was used with N-methyl-2,4,6-trichlorobenzamide and with the trinitro analog.[13] The treatment of N-methyl-3-chlorobenzamide and the 4-isomer with 100% nitric acid[10] at ice temperature resulted in substitution on the ring and on the amide nitrogen.

Extrapolation of this series of reactions for the purpose of predicting the position of nitration in other monosubstituted and unsubstituted N-methylbenzamides leads to conclusions: (a) ring nitration is expected to occur under conditions favoring nitryl ion (NO_2^+) formation, *viz.*, nitric and sulfuric acids[14]; (b) N-nitration can be expected only if the absence of deactivating groups on the ring renders the amide nitrogen sufficiently more electron rich to permit nitration employing fuming nitric acid and acetic anhydride[15] or copper nitrate and acetic anhydride.[16] Under these conditions acetyl nitrate is the nitrating species and is considered milder than the nitric acid–sulfuric acid mixture.

Nitration of Monosubstituted N-Methylbenzamides.—N-Methylbenzamides were chosen for nitration due

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[1] Taken in part from the M.S. thesis of C. J. Peterson, 1962; presented at the 1962 Waverly Meeting, Iowa Academy of Science.

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TABLE I

PREPARATION OF N-METHYLBENZAMIDES

X	M.p., °C. Found	M.p., °C. Reported	Yield, %	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
-H	82	82[a]	46	71.12	6.66	10.37	71.42	6.64	10.35
2-Br	142		80	44.86	3.74	6.54	44.80	3.71	6.45
3-Br	92		79	44.86	3.74	6.54	44.59	3.64	6.66
4-Br	164		83	44.86	3.74	6.54	44.95	3.75	6.40
2-Cl	122	122[b]	88	56.64	4.72	8.26	56.80	4.96	8.55
3-Cl	77	75[b]	80	56.64	4.72	8.26	56.45	4.92	8.09
4-Cl	161	161[b]	86	56.64	4.72	8.26	56.81	4.59	7.96
3-F	93		61	62.75	5.23	9.15	62.25	4.99	9.53
4-F	132		86	62.75	5.23	9.15	62.64	5.58	9.41
2-I	151		84	36.78	3.07	5.36	36.84	3.06	4.98
3-I	105		82	36.78	3.07	5.36	36.92	3.30	5.43
4-I	165		87	36.78	3.07	5.36	36.84	3.25	5.08
3-NO_2	175	174[c]	85	53.34	4.44	15.56	53.42	4.56	15.64
4-NO_2	220	218[c]	67	53.34	4.44	15.56	53.47	4.30	15.48
4-CH_3	146	146[d]	60	72.49	7.38	9.39	72.36	7.08	9.48
4-OCH_3	118	116[e]	65	65.45	6.67	8.48	65.52	6.29	8.85
2-OH	89	90[f]	32	63.58	5.96	9.27	63.41	6.02	8.93

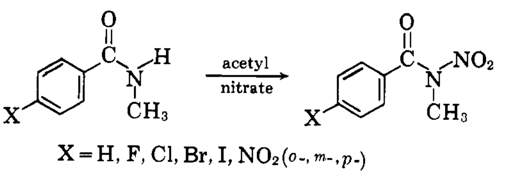
[a] Ref. 17. [b] Ref. 10. [c] Ref. 18. [d] Ref. 12. [e] Ref. 19. [f] Ref. 20.

to the ease of their preparation in a pure state and because the N-methyl-N-nitro compounds were expected to be more stable than nitroamides with other N-alkyl groups. A number of monosubstituted N-methylbenzamides have not been reported previously in the literature. The amides were prepared by the unambiguous Schotten–Bauman reaction, with the results listed in Table I.

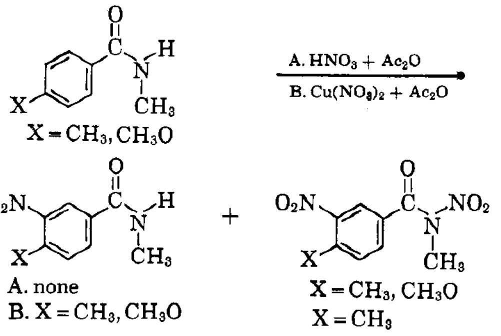
The nitration conditions applied to the amides involved two nitrating mixtures: acetic anhydride with fuming nitric acid and acetic anhydride with copper(II) nitrate. In both mixtures the nitrating species is acetyl nitrate.[15,16,21]

Careful temperature control was maintained. During the mixing of the reagents, the temperature was held well below the subsequent reaction temperature. This avoids the possibility of local temperature rises due to heat of mixing, which could allow initiation of the exothermic nitration. The chain reaction resulting from this would rapidly get out of hand. After the mixing was completed, the reactions occurred smoothly at 0° with fuming nitric acid–acetic anhydride; the copper nitrate–acetic anhydride reaction mixtures were allowed to warm to room temperature for completion.

Predominant N-nitration occurred in the cases of N-methylbenzamide and the monohalogen and mononitro substituted N-methylbenzamides, and in excellent yields. Difficulty was experienced in isolating the fluoro analogs, resulting in low yields. No ring nitration products could be detected in any of these cases.



The nitration of 4-methoxy-N-methylbenzamide with copper nitrate–acetic anhydride resulted in ring substitution to give 3-nitro-4-methoxy-N-methylbenzamide. With fuming nitric acid–acetic anhydride, N,3-dinitro-4-methoxy-N-methylbenzamide was formed. Nitration of N,4-dimethylbenzamide gave two products by ring and N-nitration: N,3-dinitro-N,4-dimethylbenzamide and 3-nitro-N,4-dimethylbenzamide.



The structures of the nitration products were established by elemental analysis, hydrolysis, infrared spectra, and reductive cleavage. The hydrolysis reaction cleaved the amide bond to yield the carboxylic acid.[22-31] If nitration occurred on the amide nitrogen, the acid recovered from the hydrolysis would carry only the substituent originally present before nitration, whereas a nitro group introduced onto the ring in the nitration step would survive the hydrolysis and appear in the carboxylic acid. The latter result occurred only in the case of the nitration products from the 4-methyl- and 4-methoxyl-N-methylbenzamides. Dinitration was detected by elemental analysis.

The infrared spectra of the N-methyl-N-nitrobenzamides show the expected absorption bands: absence of the N—H band in the 3300-cm.$^{-1}$ region; C=O band at 1708–1716 cm.$^{-1}$; and N-nitro asymmetric and sym-

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(17) H. L. Wheeler, *Am. Chem. J.*, **23**, 139 (1900).
(18) J. J. Blanksma, *Rec. trav. chim.*, **21**, 417 (1902).
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(23) T. Zincke, *Ber.*, **7**, 1502 (1874).
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(26) N. V. Sidgwick and E. K. Ewbank, *J. Chem. Soc.*, 119, 981 (1921).
(27) A. F. Holleman, *Rec. trav. chim.*, **25**, 332 (1906).
(28) P. Greiss, *Ber.*, **4**, 522 (1871).
(29) V. von Richter, *ibid.*, **4**, 553 (1871).
(30) A. Naumann, *Ann.*, **133**, 205 (1865).
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metric bands at 1575–1593 cm.$^{-1}$ and 1320–1334 cm.$^{-1}$, respectively. A more detailed study of the infrared spectra is being conducted.

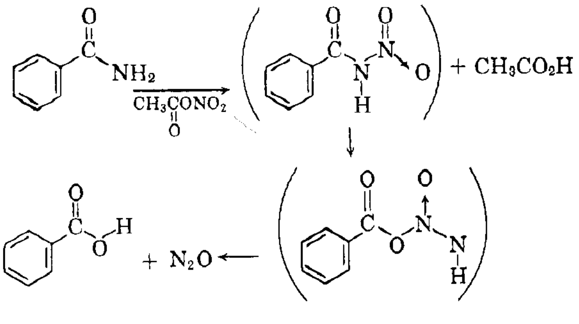
Reductive cleavage of three of the N-methyl-N-nitrobenzamides occurred upon treatment with zinc and acetic acid, or stannous chloride. The nitrogen–nitrogen bond was cleaved, yielding the N-methylbenzamide. The hydrazide which would have resulted from simple reduction of the nitro group was not found.

Nitration of benzamide was studied, employing the two classes of nitrating agents. With those nitrating agents in which the nitryl ion ($^+NO_2$) is the nitrating species, only nuclear nitration occurred. Thus, with potassium nitrate and concentrated sulfuric acid and with fuming nitric acid and fuming sulfuric acid, nearly quantitative yields of *m*-nitrobenzamide were obtained. Under these nitrating conditions no cleavage of the amide bond occurred. With fuming nitric acid and concentrated sulfuric acid, benzamide was recovered unchanged.

Treatment of benzamide with nitrating agents of the acetyl nitrate class, *viz.*, fuming nitric acid and acetic anhydride or cupric nitrate and acetic anhydride, resulted in the formation of benzoic acid in 87–93% yield. When the reaction time was sharply reduced to five minutes, a mixture of benzoic acid (57%) and benzamide (28%) was formed. *The half-life of the benzoic acid formation reaction is, therefore, less than five minutes.*

In view of the fact that no amide cleavage occurs when benzamide is treated with strong nitrating agents, the benzoic acid which is formed under milder nitrating conditions cannot be explained rationally by a simple hydrolysis.

The only rational conclusion to be obtained from these results is that, with acetyl nitrate reagents, nitration occurs at the amide nitrogen with subsequent rapid rearrangement of the intermediate N-nitrobenzamide to the corresponding benzoic acid, either *via* the less stable diazoxy ester or by direct cleavage of the N-nitrobenzamide with assistance from the solvent.



Experimental

Synthesis of N-methylbenzamides.—All amides were prepared according to the Schotten–Bauman reaction. The synthesis of N-methyl-4-chlorobenzamide will serve to illustrate the method.

Thirty-two grams (0.2 mole) of 4-chlorobenzoic acid was put in a flask, 28 ml. (0.4 mole) of redistilled thionyl chloride (b.p. 75–76°) was added in one batch, and the mixture was heated gently for 8–10 hr. After cooling, two 20-ml. portions of benzene were added and following each addition the volatile material (an azeotrope of thionyl chloride and benzene) was removed with the aid of an aspirator vacuum. To a mixture of a 10% aqueous sodium hydroxide solution containing 8 g. (0.2 mole) of sodium hydroxide and 35 ml. of 40% aqueous methylamine was added the acid chloride with stirring. Oily drops appeared immediately. After the addition was complete the solution was stirred for 30 min. The solution was poured on ice (*ca.* 200 ml.) and stirred until the oil hardened into a solid mass. The product was collected on a filter, dried, and recrystallized from a water–ethanol pair. Twenty-nine grams (86%) of a white product melting at 161° was obtained.

The results are listed in Table I.

Synthesis of N-methyl-N-nitrobenzamides.—The N-methyl-N-nitrobenzamides were prepared by two different methods. Each will be illustrated for the preparation of N-methyl-N-nitro-3-bromobenzamide.

A.—Using a Dry Ice–acetone cooling bath, 50 ml. of acetic anhydride was cooled to −15°. Fuming nitric acid (Sp. Gr. 1.49–1.50, 25 ml.) was added drop by drop keeping the temperature between −10 to −15°. A mixture of 10.3 g. (0.048 mole) of N-methyl-3-bromobenzamide and about 25 ml. of acetic anhydride was added slowly at −15° with vigorous stirring. The mixture was allowed to warm up to 0° and maintained at 0 to 4° for 10 hr. The reaction mixture was poured on 300 ml. of ice and stirred until a precipitate formed. The product was isolated by filtration and recrystallized from petroleum ether (30–60°). The purified product, consisting of shiny white platelets melting at 53°, weighed 7 g. (56%).

Hydrolysis of the product with 20% sodium hydroxide produced on acid melting at 154°. A mixture melting point with an authentic sample of 3-bromobenzoic acid was not lowered.

B.—Half of a solution of 5 g. (0.024 mole) of N-methyl-3-bromobenzamide in 15 ml. of acetic anhydride was added slowly with stirring to a cooled solution (8–10°) of 2.2 g. (0.009 mole) of copper nitrate trihydrate in 15–20 ml. of acetic anhydride. More copper nitrate trihydrate (2.2 g., 0.009 mole) and the rest of the amide solution was added. After the final addition the solution was stirred for 2 hr. at 0–4° and then for 2 hr. at room temperature. The copper salts were removed by filtration. The filtrate was poured on 50 g. of ice. The oil which precipitated solidified after 15–20 min. After recrystallization from petroleum ether (30–60°) the product, obtained as shiny white platelets, weighed 5 g. (81%) and melted at 53°.

The results are listed in Table II.

Hydrolysis of N-Methyl-N-nitrobenzamides.—Approximately 0.3 g. of the nitroamide was hydrolyzed by boiling in 20% aqueous sodium hydroxide for 10–15 min. The solution was acidified with dilute hydrochloric acid sufficient to precipitate the acid. Mixture melting points of the acids produced with authentic samples of the acids were not lowered. The results are listed in Table II.

Reductive Cleavage of N-Methyl-N-nitrobenzamides. A. With Zinc and Acetic Acid.—To a stirred mixture of 3 g. of glacial acetic acid and 5 ml. of distilled water were added alternately in small portions 2 g. (0.0077 mole) of N-methyl-N-nitro-4-bromobenzamide and 3.5 g. (0.054 mole) of zinc dust, at 0°. The mixture was allowed to warm to room temperature and was stirred for 3 hr. The product isolated by ether extraction weighed 1.6 g. (98%) and melted at 163–164°. The melting point was not depressed upon admixture with authentic N-methyl-4-bromobenzamide.

B. With Stannous Chloride and Concentrated Hydrochloric Acid.—To a stirred solution of 3.18 g. (0.014 mole) of stannous chloride trihydrate in 7 ml. of concentrated hydrochloric acid was added in one batch 1 g. (0.0046 mole) of N-methyl-N-nitro-4-chlorobenzamide. The temperature rose very slowly at first and then quite rapidly. The mixture was cooled and poured into 30 ml. of 40% aqueous sodium hydroxide solution; ice was added to keep the temperature at 4°. The product which precipitated immediately was collected on a filter, washed with distilled water, and recrystallized from water. A yield of 0.8 g. (95%) of a product melting at 157° was obtained. The melting point was not depressed upon admixture with authentic N-methyl-4-chlorobenzamide.

The same procedure applied to the 4-fluoro compound yielded 95% of N-methyl-4-fluorobenzamide.

Nitration of N,4-Dimethylbenzamide. A.—The fuming nitric acid–acetic anhydride nitration procedure (method A) was applied to 15 g. (0.10 mole) of N,4-dimethylbenzamide. The product was isolated by filtration and recrystallized twice from diethyl ether. The purified product, N,4-dimethyl-N,3-dinitrobenzamide, consisting of yellow crystals, m.p. 92°, weighed 15.2 g. (78%).

Anal. Calcd. for $C_9H_9N_3O_5$: C, 45.18; H, 3.77; N, 17.57. Found: C, 45.14; H, 4.00; N, 17.56.

TABLE II

PREPARATION OF N-NITROBENZAMIDES

X	M.p., °C.	Yield,[a] %	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	M.p. of acids, °C.[b]
-H	63	63 A 75 B	53.34	4.44	15.56	53.34	4.63	15.55	122 (22)
2-Br	53	71 A	37.07	2.70	10.81	37.14	2.85	11.04	148 (23)
3-Br	53	56 A 81 B	37.07	2.70	10.81	37.13	2.67	10.50	155 (24)
4-Br	81	75 A	37.07	2.70	10.81	37.33	3.06	10.92	253 (25)
2-Cl	66	73 A	44.76	3.26	13.06	44.82	3.33	13.19	142 (10)
3-Cl	47	83 A	44.76	3.26	13.06	44.91	3.39	13.15	155 (26)
4-Cl	65	63 A 71 B	44.76	3.26	13.06	44.88	3.27	13.13	240 (26)
3-F	27	30 A	48.49	3.54	14.14	[c]			123 (27)
4-F	51	89 A	48.49	3.54	14.14	48.48	3.17	14.29	181 (27)
3-I	73	64 A	31.38	2.29	9.15	31.66	2.23	9.24	185 (28)
4-I	101	76 A	31.38	2.29	9.15	31.53	2.58	9.06	266 (29)
3-NO_2	63	66 A 80 B	42.67	3.11	18.67	42.87	3.29	18.65	138 (30)
4-NO_2	58	74 A 48 B	42.67	3.11	18.67	42.76	3.30	18.69	234 (31)

[a] Procedure employed is indicated: A, fuming nitric acid in acetic anhydride, and B, cupric nitrate in acetic anhydride. [b] Numbers in parentheses are literature references for acids resulting from hydrolysis of N-nitrobenzamide. [c] Unstable.

Basic hydrolysis of this compound with 20% aqueous sodium hydroxide followed by acidification produced an acid melting at 188° (3-nitro-4-methylbenzoic acid, m.p. 189–190°).[32]

B.—The copper nitrate–acetic anhydride nitration procedure (method B) was applied to 4 g. (0.027 mole) of N,4-dimethylbenzamide. After the reaction was complete, the copper salts were removed by filtration. The filtrate was poured on 50 ml. of ice. The oil which precipitated partially solidified after 5 days. Fractional recrystallization from petroleum ether (30–60°) separated this oil into two solid products: (1) 2.8 g. (43%) of N,4-dimethyl-N,3-dinitrobenzamide, m.p. 92°, (a mixture melting point with an authentic sample of the compound was not lowered); and (2) 1.7 g. (32%) of N,4-dimethyl-3-nitrobenzamide, m.p. 148° (lit.[12] m.p. 148°).

Basic hydrolysis of either product followed by acidification produced an acid melting at 188° (3-nitro-4-methylbenzoic acid, m.p. 189–190°).[32]

Nitration of N-Methyl-4-methoxybenzamide. A.—In the usual manner 12 g. (0.073 mole) of N-methyl-4-methoxybenzamide was allowed to react with a mixture of 50 ml. of acetic anhydride and 25 ml. of fuming nitric acid. The yellow crystalline product N-methyl-N,3-dinitro-4-methoxybenzamide after two recrystallizations from petroleum ether (b.p. 30–60°) melted at 105° and weighed 8.6 g. (56%).

Anal. Calcd. for $C_9H_9N_3O_6$: C, 42.35; H, 3.53; N, 16.47. Found: C, 42.54; H, 3.64; N, 16.11.

Basic hydrolysis of the product followed by acidification produced an acid melting at 187° (3-nitro-4-methoxybenzoic acid, m.p. 186–187°[33]; 4-methoxybenzoic acid, m.p. 185°).[34] A mixture melting point with an authentic sample of 4-methoxybenzoic acid was lowered.

B.—Half of a solution of 5 g. (0.030 mole) of N-methyl-4-methoxybenzamide in 10 ml. of acetic anhydride was added slowly with stirring to a cooled solution (8–10°) of 3.2 g. (0.013 mole) of cupric nitrate trihydrate in 15 ml. of acetic anhydride. More cupric nitrate (3.2 g., 0.013 mole) and the rest of the amide solution was added. After the final addition the solution was stirred for 2 hr. at 0–4° and then for 2 hr. at room temperature. The copper salts were removed by filtration. The filtrate was poured on 50 ml. of ice and the solid precipitate collected on a filter. Three grams (47%) of N-methyl-3-nitro-4-methoxybenzamide melting at 138° was obtained after recrystallization from water.

Basic hydrolysis of the product followed by acidification produced an acid melting at 188° (3-nitro-4-methoxybenzoic acid, m.p. 186–187°).[33]

TABLE III

ULTRAVIOLET SPECTRA OF N-NITRO-N-METHYLBENZAMIDES

X	λ_{max}, Å.	$\epsilon \times 10^{-3}$
-H	2480	76
2-Br	2400	9
3-Br	2510	46
	2920 sh	
4-Br	2610	28
2-Cl	2440	17
3-Cl	2490	7.2
4-Cl	2580	11.7
3-F	2430	9.8
4-F	2260	12.7
3-I	2470	15.5
	3000 sh	
4-I	2780	11.4
3-NO_2	2480	15.4
	2910 sh	
4-NO_2	2560	44
4-CH_3-3-NO_2	2370	5.7
4-OCH_3-3-NO_2	2440	10.8
	2750	8.2

TABLE IV

INFRARED SPECTRA OF N-NITRO-N-METHYLBENZAMIDES

Ring subst.	Assignments, cm.$^{-1}$ C=O	N—NO_2	C—NO_2	NO_2
-H	1711	1570		1323
2-Br	1710	1593		1335
3-Br	1712	1575		1323
4-Br	1712	1578		1320
2-Cl	1710	1595		1334
3-Cl	1708	1578		1322
4-Cl	1713	1579		1323
3-F	1716	1580		1326
4-F	1708	1572		1320
3-I	1714	1580		1325
4-I	1710	1583		1323
3-NO_2	1716	1584	1542	1351
4-NO_2	1710	1580	1532	1345
4-CH_3-3-NO_2	1710	1577		1345

Nitration of N-Methyl-2-hydroxybenzamide.—Two attempts at nitration of this compound *via* the usual nitration procedures produced only a deep red solution from which no product could be isolated.

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(32) F. Fittica, *Ann.*, **172**, 309 (1874).

(33) H. Salkowski, *ibid.*, **163**, 8 (1872).

(34) E. E. Harris and G. B. Frankforter, *J. Am. Chem. Soc.*, **48**, 3149 (1926).

Nitration of Benzamide.—A solution of 10 g. (0.08 mole) of finely powdered benzamide in 55 ml. of sulfuric acid was stirred at 15°. To this was added 8.4 g. of potassium nitrate (0.03 mole). The mixture was stirred at room temperature for 3 hr. The product isolated by pouring the mixture onto 400 g. of ice weighed 12.3 g. (89%) and melted at 143° (3-nitrobenzamide, m.p. 143°).[18,35] Basic hydrolysis followed by acidification produced an acid melting at 140° (3-nitrobenzoic acid, m.p. 140°).[30] A mixture melting point with an authentic sample of 3-nitrobenzoic acid was not lowered.

B.—To 35 ml. of fuming nitric acid (Sp. Gr. 1.49) decolorized with urea, was added 10 g. of finely powdered benzamide. Fuming sulfuric acid (17 ml.) was added slowly with stirring at 0°. The mixture was stirred for 10 min. and poured onto ice. There was isolated 12.6 g. (92%) of product melting at 143°. A mixture melting point with an authentic sample of 3-nitrobenzamide was not lowered. Substitution of concentrated sulfuric acid for fuming sulfuric acid resulted in the recovery of unaltered benzamide [9.7 g. (98%), m.p. 126°]. A mixture melting point with an authentic sample of benzamide was not lowered.

C.—The product obtained by allowing 10 g. of benzamide to react with a fuming nitric acid–acetic anhydride mixture for 10 hr. at 0° weighed 9.4 g. (93%) and melted at 120° (benzoic acid, m.p. 121°).[22] A mixture melting point with an authentic sample of benzoic acid was not lowered. When the reaction time was reduced to 15 min., 9.1 g. (90%) of benzoic acid was obtained.

D.—Benzamide was treated with an acetic anhydride-cupric nitrate trihydrate mixture for 2 hr. at 0°; the product isolated weighed 8.8 g. (87%) and melted at 119°. A mixture melting point with benzoic acid was not lowered. When the reaction was allowed to proceed for only 5 min. two products were isolated: (1) benzamide, 2.8 g. (28%), m.p. 127°; and (2) benzoic acid, 5.1 g. (57%), m.p. 122°.

Nitration of 3-Nitrobenzamide.—Treatment of 10 g. of 3-nitrobenzamide with fuming nitric acid–fuming sulfuric acid as before yielded 9 g. of unaltered starting material, identified by mixture melting point.

Measurement of Spectra.—The ultraviolet measurements were made on a Cary Model 11 recording spectrophotometer from 4000–2400 Å. Samples were run in isooctane at molar concentrations of 1×10^{-4} and 1×10^{-5} in a 1-cm. silica cell with matched blank solvent cell. Representative spectra are listed on Table III.

The Perkin-Elmer Model 21 double-beam spectrophotometer was used to obtain the infrared data. The spectra were run in carbon tetrachloride at a concentration of 15 mg./ml. in 0.1-mm. sodium chloride cells (see Table IV).

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[35] E. Reid, *Am. Chem. J.*, **21**, 290 (1899).

The Products of the Reactions of Sodium *t*-Butylmercaptide with Vinyl Chloride, Vinylidene Chloride, and *cis*- and *trans*-Dichloroethylenes[1,2]

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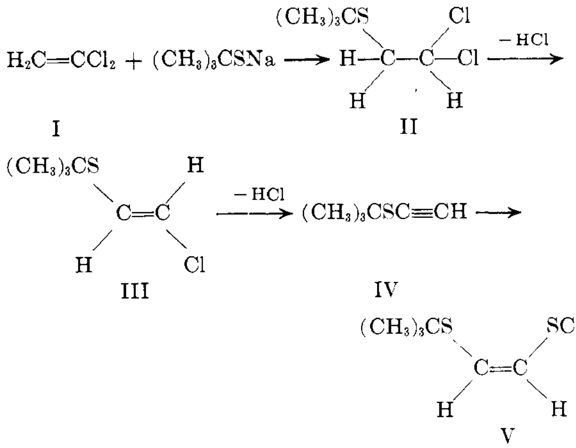
The products of the reactions of alcoholic sodium *t*-butylmercaptide with vinyl chloride, vinylidene chloride, and *cis*- and *trans*-dichloroethylenes are described.

Previous work in this laboratory on nucleophilic reactions of *p*-toluenethiolate[2] and *p*-tolueneselenolate[3] reagents with haloethylenes has been extended to an aliphatic thiolate,[4] sodium *t*-butylmercaptide. The major reaction paths were found to be the same as those observed with *p*-toluenethiolate and *p*-tolueneselenolate,[4] *i.e.*, elimination–addition with vinyl chloride and *cis*- and *trans*-dichloroethylene, and addition-elimination with vinylidene chloride. One difference resulted from the greater basicity of sodium *t*-butylmercaptide. Whereas, in the reaction of *cis*-dichloroethylene with *p*-toluenethiolate, excess sodium ethoxide is required for initial dehydrohalogenation, sodium *t*-butylmercaptide is sufficiently basic to effect initial dehydrohalogenation.

Vinyl Chloride.—Vinyl chloride reacts with sodium *t*-butylmercaptide in the presence of sodium ethoxide at elevated temperatures to give *t*-butylmercaptoethene, presumably by the elimination–addition sequence observed with aromatic thiolates.[2]

$$CH_2{=}CHCl + (CH_3)_3CSNa \xrightarrow[\Delta]{EtONa} HC{\equiv}CH \longrightarrow (CH_3)_3CSCH{=}CH_2$$

Vinylidene Chloride.—By analogy to the reaction with sodium *p*-toluenethiolate, it would be predicted that the first step in the reaction of sodium *t*-butylmercaptide with vinylidene chloride should be addition followed by elimination. In fact vinylidene chloride is comparatively resistant to dehydrohalogenation.[2] In further agreement with this hypothesis is the isolation of 1,1-dichloro-2-(*t*-butylmercapto)ethane (II) together with *trans*-1-chloro-2-(*t*-butylmercapto)ethene (III) from the reaction of vinylidene chloride with sodium *t*-butylmercaptide at 50°.



When vinylidene chloride is treated with sodium *t*-butylmercaptide at 100°, *trans*-1-chloro-2-(*t*-butylmercapto)ethene (III) and *cis*-1,2-bis(*t*-butylmercapto)ethene (V) are isolated from the reaction mixture.

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[1] For preceding paper see W. E. Truce and B. Groten, *J. Org. Chem.*, **27**, 128 (1962).

[2] Nucleophilic replacements from olefinic carbons have been summarized by several authors, *e.g.*, N. Kharasch, "Organic Sulfur Compounds," Ed., W. E. Truce, Chap. 12, Pergamon Press, New York, N. Y., 1961; Abstracts, 17th National Organic Chemistry Symposium of the American Chemical Society, 1961.

[3] G. R. Price, Ph.D. thesis, Purdue University, Lafayette, Ind. (1959).

[4] Some over-all reactions of aliphatic thiolates with a few vinylic halides and thioacetylenes have been studied previously, J. F. Arens, *Advan. Org. Chem.*, **2**, 117 (1960).