PREPARATION
OF
CERTAIN ORGANIC COMPOUNDS
OF NITROGEN

THE PREPARATION OF CERTAIN ORGANIC COMPOUNDS OF NITROGEN

I. 2,4-Dinitraniline

II. Nitromethane

III. Methyl Urea

THESIS

Presented to The Faculty of Graduate Studies and Research in partial requirement for the degree of Master of Science.

by

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ACKNOWLEDGMENT

The writer wishes to express his indebtedness and gratitude to Dr. C. F. H. Allen whose kindly advice has made this work possible.

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I.

The Preparation of 2,4-dinitraniline.

INTRODUCTION

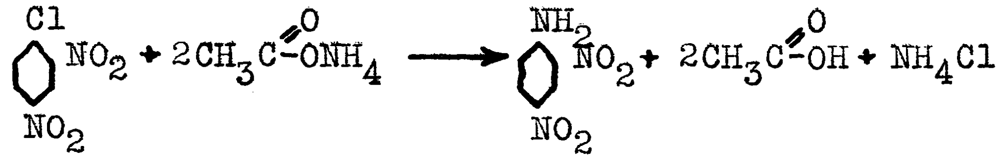
All previous methods of preparative value for 2,4-dinitraniline have required the use of sealed tubes or autoclaves. The starting materials have been 2,4-dinitrochlorbenzene and ammonia in some form, usually in aqueous or alcoholic solution. This type of reaction is inconvenient for the ordinary laboratory, and the purpose of this work was to develop a better method.

It was thought that if the boiling point of the mixture could be raised sufficiently and still keep the ammonia in solution, the reaction would take place without a closed apparatus. As a suitable source of ammonia, ammonium acetate was selected. A little glacial acetic acid was added as solvent. A satisfactory method was developed and the results are recorded in the experimental part.

The use of urea was also considered and found to be practically as good; acetamide was unsatisfactory.

Equations for the two methods of preparation are:-

1.



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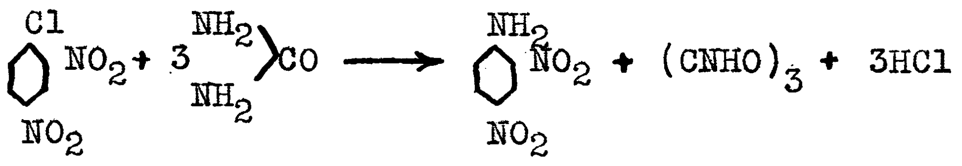


HISTORICAL

Clemm[1] found that when 2,4-dinitro-chlorbenzene and ammonium hydroxide were heated in a closed tube for five hours at 100°-120° C., 2,4-dinitraniline was obtained.

Salkowski[2] found that by heating 2,4-dinitro-anisol or 2,4-dinitro-anisic acid with aqueous or alcoholic ammonia in a closed tube for six hours on a water bath, 2,4-dinitraniline with a melting point of 172°-174°C. resulted.

Willgerodt[3] heated 2,4-dinitro-chlorbenzene with ammonium hydroxide in a sealed tube at 100°-130°C. and obtained 2,4-dinitraniline with a melting point of 181°-182°C.

Hepp[4] prepared 2,4-dinitraniline with a melting point of 175°C. by the action of alcoholic ammonia on 2,4-dinitro-chlorbenzene.

Van Romburgh[5] found that adding a slight excess of an amine in alcoholic solution to 2,4-dinitro-brombenzene, also in alcoholic solution produced a substituted dinitro-amine. Ammonia, however, would not give an unsubstituted amine.

Barr[6] obtained 2,4-dinitraniline by heating 2,4-dinitro-phenol and 27% ammonium hydroxide for seven hours at 170°C.

Bamberger[7] found that p-nitro nitroamine rearranges on standing to give 2,4-dinitraniline.

Hoff[8] found that on treating the same substance with sulphuric acid at 0°C. 2,4-dinitraniline resulted.

Kenner[9] showed that dinitro-chlorbenzene is much more active than mononitro-chlorbenzene so that the chlorine can be more easily replaced by an amino group.

Sprung[10] has shown that a trinitro halide of benzene is twenty five times more active thane a dinitro halide which is in turn two thousand times more active than a mononitro halide.

Kym[11] heated 2,4-dinitro-chlorbenzene and acetamide in a sealed tube at 200°-210°C. for seven hours. He obtained 2,4-dinitro-acetanilid which he treated with potassium hydroxide until it turned red and then heated the mixture for several hours. On cooling and purifying, the crystals were found to be 2,4-dinitraniline.

Pfister[12] prepared 2,4-dinitraniline by heating urea and 2,4-dinitro-chlorbenzene together.

EXPERIMENTAL

A. Use of ammonium acetate and acetic acid.

10 grams of 2,4-dinitro-chlorbenzene, 40 grams of ammonium acetate, and five cc. of glacial acetic acid were mixed and placed in a flask fitted with a reflux condenser. The flask was heated to 155°C. for eight hours on an oil bath. It was then cooled and the liquid filtered from the solid which was then boiled in water and cooled again. The solid was again filtered and dissolved in as little alcohol as possible at the boiling point. Water was added until the solution became turbid whereupon it was again heated until clear. At this point many of the subsequent were filtered to free them of material which was insoluble both in pure alcohol and in the alcohol and water mixture. The solution was then cooled and the crystals filted off. They were brown in color with a melting point of 175°-177°C. and a mixed melting point with pure 2,4-dinitraniline showed no depression. They were thus proven to be 2,4-dinitraniline as was expected. The yeild was 2.5 grams or about 28% of the theoretical yield.
When more water was added to the filtrate, a mass of light yellow crystals was precipitated. 2.5 grams of this new material was obtained and set aside for further investigation.

A series of runs showed that a large excess of ammonium acetate was no advantage and that heating must proceed for the eight hours; see table of results on page 7.

A run was made with the omission of acetic acid and the yield was 4 grams (45%) of 2,4-dinitraniline and 2 grams of the unidentified substance. Further runs without the use of acetic acid as solvent gave yields as high as 61% of the theoretical; see page 7.

Since a decrease in the amount of free acetic acid present seemed to have the effect of increasing the yield, an attempt was made to still further decrease the acid content of the reaction mixture by passing a continuous stream of ammonia through it during the reaction to convert the acetic acid to ammonium acetate as fast as it was liberated. A diagram of the apparatus which was used and which proved to be satisfactory is given on page 6.

By the use of this apparatus the yield was raised to 75%-80% with about 10% of the unidentified material; the remaining 10% was lost in washing as evidenced by the yellow color of all filtrates and washing solutions.

It was found that the time of reaction could be cut down to six hours and that only one-half of the ammonium acetate theoretically necessary to convert 2,4-dinitro-chlorbenzene to 2,4-dinitraniline was enough in this apparatus. The rate at which ammonia was passed was 3-4 bubbles per second as shown in the bubble counter; see page 7.

A run was made with refined 2,4-dinitro-chlorbenzene instead of the technical material previously employed, and the result was that only a trace of the unidentified substance was obtained. It was thus proven that this foreign product was caused by impurities in the starting materials. The reason suggested for the decrease of unidentified substance with increased yield was that more of the unknown was carried down with the larger mass of 2,4-dinitraniline.

Diagram of the apparatus used in the production of
2,4-dinitraniline.

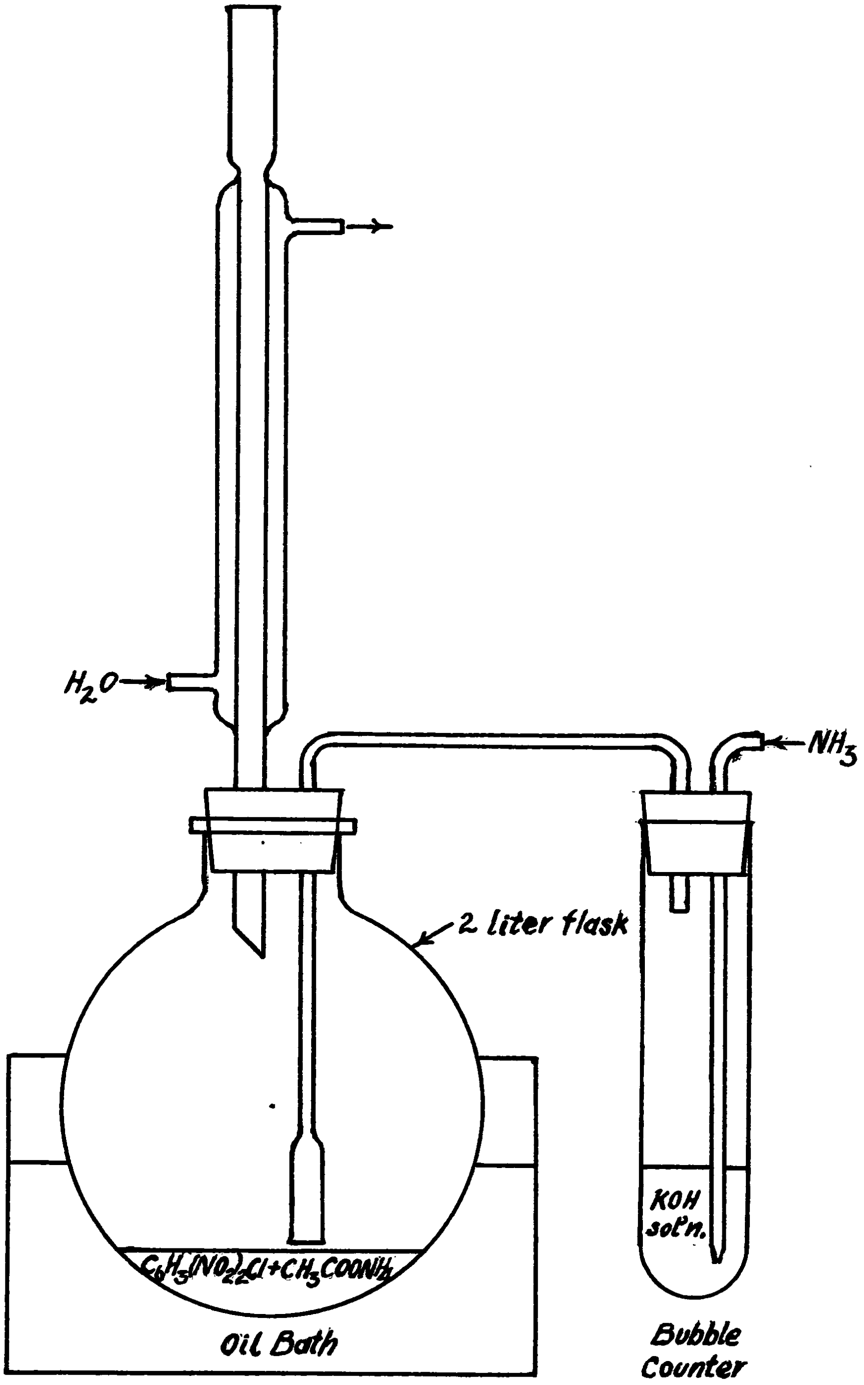


Table II. RESULTS OBTAINED IN THE PREPARATION OF NITROMETHANE

Run	Gms. $CH_2ClCOOH$	Gms. $NaNO_2$	Gms. NaOH	Gms. added material	1st. distillation		2nd. distillation		3rd. distillation		Total c.c. CH_3NO_2	Gms. CH_3NO_2	% yield based on[1]		Remarks	Notes[2]
					c.c. H_2O	c.c. CH_3NO_2	c.c. H_2O	c.c. CH_3NO_2	c.c. H_2O	c.c. CH_3NO_2			$NaNO_2$	$CH_2ClCOOH$		
1	100	60	43	-	225	10	92	19	29	4	33	33	50.5	41.5	-	a
2	100	60	43	-	230	10	100	19	30	4	33	33	50.5	41.5	-	a
3	100	60	43	-	270	10	150	21	60	9	40	36	55.1	46.1	-	b
4	100	60	43	1 gm. LiCl	265	10	140	21	38	5	36	34	52.0	42.8	-	a
5	100	60	43	1 gm. LiCl	260	10	100	20	35	5	35	32.5	49.8	41.0	-	b
6	100	60	43	60 gms. boric acid	275	1	120	21	36	4	26	25	38.4	31.4	-	a
7	100	60	45	60 gms. boric acid	500	1	200	26	104	10	37	35	53.7	44.1	Boric acid added to $CH_2ClCOOH$	a;c
8	100	60	45	60 gms. boric acid	400	4	120	23	34	6	33	32	49.0	40.3	Boric acid added to $CH_2ClCOOH$	b;c
9	100	60	43	60 gms. boric acid	400	0	110	25	35	8	33	32	49.0	40.3	Boric acid added to $CH_2ClCOONa$	a;c
10	100	60	43	60 gms. boric acid	445	1	103	25	40	6	32	31	47.4	39.1	Boric acid added to $CH_2ClCOONa$	b;c
11	100	60	43	332 gms. borax	240	7	90	18	30	4	29	28	42.9	35.2	-	a
12	100	60	43	332 gms. borax	270	9	92	18	35	4	31	30	46.0	37.8	-	b
13	100	60	43	37 gms. LiCl	254	12	93	18	32	5	35	33	50.5	41.5	-	b
14	100	60	--	-	250	9	92	20	33	5	34	32	49.0	40.3	Li_2CO_3 used for neutralization	b
15	100	60	--	-	254	10	95	16	33	7	33	31	47.4	39.1	LiOH used for neutralization	b
16	100	60	43	20 gms. soap	390	0	200	12	50	6	18	15	23.0	18.8	Foamed over on boiling	a
17	100	60	43	-	265	10	100	15	30	2	27	26	39.7	32.8	Run in CO_2 atmosphere	a
18	100	60	43	214 gms. $MgSO_4 \cdot 7H_2O$	270	16	95	15	20	2	33	33	50.5	41.5	-	b
19	100	60	43	60 gms. $(CH_2)_6N_4$	253	0	---	0	---	--	0	0	0	0	-	b
20	100	60	43	2.5 gms. gelatin	250	15	104	13	29	2	30	31	47.4	39.1	Foamed on heating	b
21	100	60	43	2 gms. $Be(NO_3)_2 \cdot 3H_2O$	280	11.5	98	18	25	3	32.5	33.5	51.4	42.1	Foamed and evolved NO_2 on heating	b
22	100	60	43	5 gms. casein	230	12	99	16	20	2	30	33	50.5	41.5	Foamed on heating	b
23	100	60	43	10 gms. Na_2SiO_3	253	12.5	110	17	20	2	31.5	33	50.5	41.5	Foamed on heating	b
24	100	60	43	1 gm. $Th(NO_3)_4$	263	10	92	20	28	2	32	34	52.0	42.8	NO_2 evolved cold; foam on heating	b
25	100	60	43	1.5 gms. $La(NH_4)_2(NO_3)_5 \cdot 5H_2O$	251	11	85	18	29	2	31	33	50.5	41.5	Foamed on heating	b
26	100	60	43	-	254	7	95	3	---	--	10	10	15.4	12.6	-	d
27	100	60	43	-	260	10	99	19	25	2	31	33	50.5	41.5	-	e
Mean													50.5	41.5	-	f

1. % yield is based on purified yield (0.812 × crude yield).

2. Key to notes given on page 19.

Table I. RESULTS OBTAINED IN THE PRODUCTION OF 2,4-DINITRANILINE FROM 2,4-DINITRO-CHLORBENZENE AND AMMONIUM ACETATE

Run	Gr. 2,4-dinitro-chlorbenzene	Gr. ammonium acetate	Temperature of reaction	Time of reaction	Yield of dinitraniline gr.	Yield of dinitraniline %	Yield of unknown gr.	Remarks
1	10	40	155 C.	8 hr.	2.5	28	2.8	-
2	10	25	160 C.	8 hr.	2.5	28	2.4	-
3	10	20	160 C.	8 hr.	0	0	0	90% 2,4-dinitro-chlorbenzene recovered.
4	10	40	160 C.	1 hr.	0	0	0	Same result.
5	10	30	170 C.	1 hr.	4	44	2	Acetic acid omitted from here on.
6	10	10	170 C.	8 hr.	4.9	54	2	-
7	20	30	170 C.	8 hr.	11	61	4.4	-
8	50	85	170 C.	8 hr.	19	42	9.8	-
9	100	110	170 C.	8 hr.	44	49	17	-
10	50	17.5	170 C.	8 hr.	34	76	1	Ammonia passed in from here on.
11	50	17.5	170 C.	8 hr.	34	76	6	-
12	50	5	170 C.	8 hr.	27	59	7	Yield contaminated with unknown.
13	50	14	170 C.	6 hr.	31	69	6	-
14	50	18	170 C.	6 hr.	35	78	0	Refined 2,4-dinitro-chlorbenzene used.

It is thus seen that the most favorable conditions for the production of 2,4-dinitraniline by this method are:

1. The use of 3.5 grams of ammonium acetate for every 10 grams of 2,4-dinitro-chlorbenzene.

2. Heating the reaction mixture at 170° C. for six hours on an oil bath.

3. Passing ammonia into the reaction flask throughout the duration of heating at the rate of 3-4 bubbles a second.

An attempt was made to apply this method to the production of p-nitraniline. 20 grams of p-nitro-chlorbenzene and 10 grams of ammonium acetate were mixed and subjected to the same conditions under which 2,4-dinitraniline was prepared. However, no p-nitraniline was obtained, and the starting materials were almost quantitatively recovered. This result was in complete accord with the work of Kenner[9] and Sprung[10].

An attempt was also made to apply this method to the production of glycine. 20 grams of monochloracetic acid and 33 grams of ammonium acetate were heated together for six hours without the addition of ammonia. The mixture was then evaporated to 50 c.c. and was a little cloudy, but the addition of 5 c.c. of water cleared it. A mixture of 80 c.c. of methyl alcohol and 14 c.c. of pyridine was added, but no crystals of glycine precipitated even after two days.

B. Use of acetamide.

10 grams of 2,4-dinitro-chlorbenzene and 3.5 grams of acetamide were heated together for eight hours at 170° C., both with and without the addition of ammonia. When no ammonia was added, no dinitraniline was produced, but a trace of it was obtained when ammonia was passed in. This was thought to be due to the direct reaction of the ammonia and the 2,4-dinitro-chlorbenzene and not to the presence of acetamide at all.

C. Use of urea.

50 grams of 2,4-dinitro-chlorbenzene and 20 grams of urea were heated on an oil bath at 170°C. for six hours. The solid mass in the flask was treated as in the case of the use of ammonium acetate, and a yield of yellow crystals was obtained which was proven to be 2,4-dinitraniline by taking a mixed melting point with an analytical sample. The yield was 32 grams or 71%.

An attempt was now made to identify the unknown substance obtained with the 2,4-dinitraniline. It was recrystallized from water several times until it had a constant melting point. The nitrogen content was then found to be 17.4% by the Kjeldahl method. The molecular weight, by the camphor method, was 165. By the use of titanous chloride, as described in directions obtained from the DuPont Co. there was found to be one nitro group to the molecule. Considerable difficulty was experienced in making carbon and hydrogen analyses, but a few of the determinations checked to give a final result of six carbons and six hydrogens so that the empirical formula came out $C_6H_6N_2O_4$. A literature search was made, and no substance could be found which corresponded to the data taken. It was then thought that the substance might contain water of crystallization which would effect the analyses. It was therefore crystallized from benzene, and a small amount of crystals, which proved to be 2,4-dinitraniline, was obtained. The benzene was evaporated down to one-fourth its original volume and ligroin was added. Yellow crystals were immediately precipitated. The original unknown substance was then examined under the microscope and found to contain two types of crystals; it must therefore have been a double salt or a eutectic mixture. The substance precipitated by ligroin had a melting point of 165°C. and a molecular weight of 182. By the titanous chloride method, it was found qualitatively to contain at least one nitro group. By diazotizing and coupling with β-naphthol and acetyl H acid, brown dyes were obtained, showing it to contain at least one amino group. As the supply of this substance was almost used up at this point, its investigation was dropped except to test for acidity. It was found to be decidedly acid, and it also gave a red color with ferric chloride which showed it to be phenolic. The unknown substance was, therefore, a nitro amino phenol; it was either originally present in or arose from an impurity in the 2,4-dinitro-chlorbenzene.

SUMMARY

2,4-dinitraniline can be satisfactorily prepared from 2,4-dinitr-chlorbenzene and ammonium acetate in the presence of ammonia gas. A yellow double compound of 2,4-dinitraniline and an unidentified nitro-amino-phenol results as a by-product when technical 2,4-dinitro-chlorbenzene is used.

2,4-dinitraniline can also be satisfactorily prepared from 2,4-dinitro-chlorbenzene and urea.

BIBLIOGRAPHY

1. Clemm, C., J. prak. Ch. (2) 1 170 (1870).
2. Salkowski, H., Ann. 174 263 (1874).
3. Willgerodt, Ber. 9 979 (1876).
4. Hepp, P., Ann. 215 362 (1882).
5. Van Romburgh, P., Rec. Trav. Chim. 4 189 (1885).
6. Barr, A., Ber. 21 1542 (1888).
7. Bamberger, E., Ber. 30 1253 (1897).
8. Hoff, E., Ann. 311 98 (1900).
9. Kenner, J., J. Chem. Soc. 105 2717-2738 (1914).
10. Sprung, M. M., J. A. C. S. 52 1650 (1930).
11. Kym, O., Ber. 32 3539 (1900).
12. Pfister, K. H. J., U. S. P. 1,752,998,
C. Abs. 24 2468 (1930).

II.

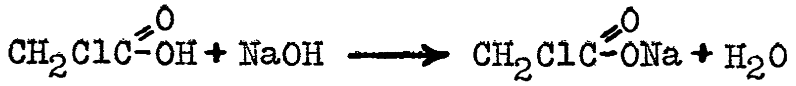
The Preparation of Nitromethane.

INTRODUCTION

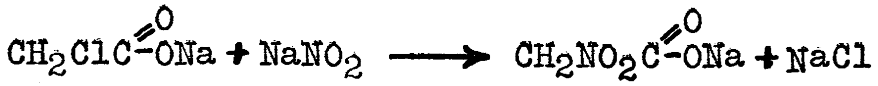
There have been many methods set fourth in the literature for the preparation of nitromethane with claims for larger yields in many cases. The object of the present work was to improve, if possible, the present methods of preparation or to find a better method than those now known.

While methods have been found giving slightly larger yields, the increase is not large enough to justify the added cost of materials.

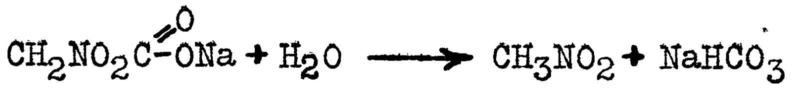
The reactions occurring in the preparation of nitromethane are:-

1. 

$$CH_2Cl\overset{O}{\overset{/\!/}{C}}-OH + NaOH \longrightarrow CH_2Cl\overset{O}{\overset{/\!/}{C}}-ONa + H_2O$$

2. 

$$CH_2Cl\overset{O}{\overset{/\!/}{C}}-ONa + NaNO_2 \longrightarrow CH_2NO_2\overset{O}{\overset{/\!/}{C}}-ONa + NaCl$$

3. 

$$CH_2NO_2\overset{O}{\overset{/\!/}{C}}-ONa + H_2O \longrightarrow CH_3NO_2 + NaHCO_3$$

The yield is materially decreased by the formation of methazonic acid in the important side reaction:-

4. $2CH_3NO_2 + NaHCO_3 \longrightarrow HON{=}CHCH{=}N(O)ONa + CO_2 + H_2O$

HISTORICAL

Nitromethane has been made by the action of potassium nitrite on potassium chloracetate (Kolbe[1] and Preibisch[3]), by the action of silver nitrite on methyl iodide (Meyer and Stuber[2] and Ray and Neogi[8]) and the products of both types of reaction proven to be identical (Meyer[4]), by the action of the corresponding sodium salts (Auger[5]), by the oxidation of methyl amine by Caro's Reagent (Bamberger[6]), by the action of potassium nitrite on dimethyl sulphate (Walden[7]), by substituting potassium carbonate for potassium hydroxide in the formation of potassium chloracetate (Steinkopf[9]), by the use of the corresponding calcium salts (Steinkopf and Kirchoff[10]), and by the use of sodium carbonate instead of potassium carbonate (Wahl[11]).

The only ones of the above methods studied were those using sodium salts in boiling aqueous solution, either alone or in the presence of other substances it was thought might be beneficial.

Whitmore and Whitmore[12] used a slightly alkaline solution of sodium chloracetate and sodium nitrite and obtained a 38% yield of nitromethane.

Alexieff and Carcanas[13] have prepared nitromethane by the action of sodium nitrite on methyl p-toluene sulphonate but did not mention the percentage yield obtained.

Hirano[14] neutralized the chloracetic acid with sodium carbonate, added sodium nitrite and sodium chloride, and steam distilled. His yield was 53%.

Wang and Tseng[15] added molar quantities of boric acid to the sodium chloracetate solution and upon reaction with sodium nitrite, obtained a 58% yield of nitromethane.

Pritzl and Adkins[16] found that a good yield could be obtained by adding a quarter of the sodium chloracetate solution to the sodium nitrite solution, heating until distillation started, and then adding the remainder of the sodium chloracetate solution slowly and continuously from a dropping funnel over a period of about fifteen minutes as distillation proceeds.

EXPERIMENTAL

In general, a standard procedure originated by Pritzl and Adkins[16] was employed:-

A solution of 60 grams of sodium nitrite in 100 c.c. of water was placed in a two liter flask fitted with a downward condenser and a dropping funnel. A solution of 100 grams of chloracetic acid in 200 c.c. of water was now neutrallized with 40% sodium hydroxide solution (43 grams of solid sodium hydroxide needed) in the cold and the resulting sodium chloracetate solution placed in the dropping funnel. The sodium nitrite solution was heated until water began to distill and the sodium chloracetate then added slowly. Nitromethane soon started to distill over with the water and was collected in the automatic separator (see diagram on page 17). The water layer was saturated with sodium chloride and redistilled; more nitromethane was thus obtained, and the water layer from this distillation, saturated with sodium chloride and distilled, gave a third small portion of nitromethane. Further "salting out" was not practical.

Many modifications were applied to this method, but no matter what the modification, all substances were added to the sodium nitrite solution unless otherwise indicated. The only general modification was that of adding one fourth of the sodium chloracetate before heating and the rest after distillation had started, as was done in the original procedure. See table of results on page 18 and notes explaining them on page 19.

Diagram of the apparatus used in the preparation of nitromethane.

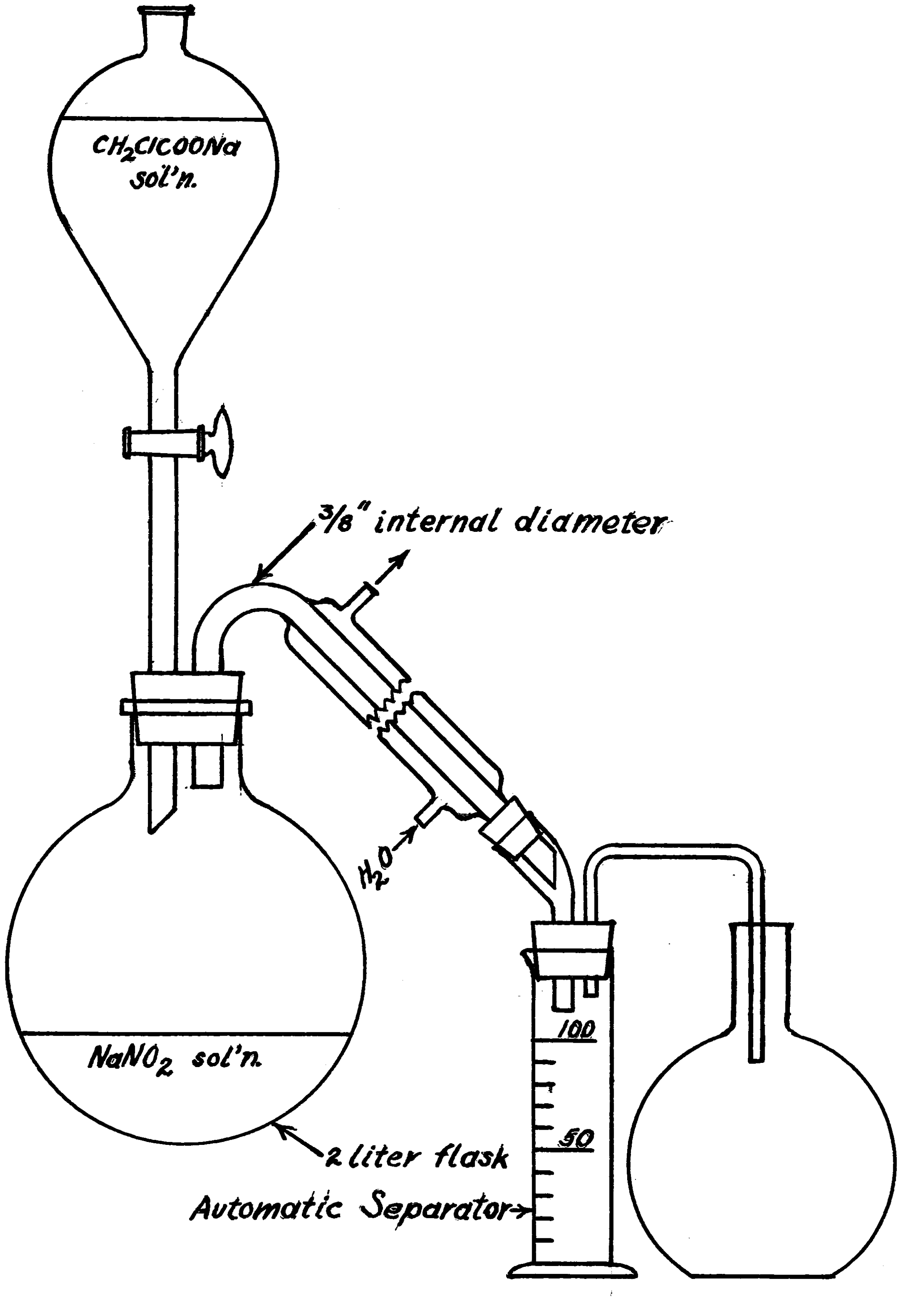


Table I. RESULTS OBTAINED IN THE PRODUCTION OF 2,4-DINITRANILINE FROM 2,4-DINITRO-CHLORBENZENE AND AMMONIUM ACETATE

Run	Gr. 2,4-dinitro-chlorbenzene	Gr. ammonium acetate	Temperature of reaction	Time of reaction	Yield of dinitraniline gr.	Yield of dinitraniline %	Yield of unknown gr.	Remarks
1	10	40	155 C.	8 hr.	2.5	28	2.8	-
2	10	25	160 C.	8 hr.	2.5	28	2.4	-
3	10	20	160 C.	8 hr.	0	0	0	90% 2,4-dinitro-chlorbenzene recovered.
4	10	40	160 C.	1 hr.	0	0	0	Same result.
5	10	30	170 C.	1 hr.	4	44	2	Acetic acid omitted from here on.
6	10	10	170 C.	8 hr.	4.9	54	2	-
7	20	30	170 C.	8 hr.	11	61	4.4	-
8	50	85	170 C.	8 hr.	19	42	9.8	-
9	100	110	170 C.	8 hr.	44	49	17	-
10	50	17.5	170 C.	8 hr.	34	76	1	Ammonia passed in from here on.
11	50	17.5	170 C.	8 hr.	34	76	6	-
12	50	5	170 C.	8 hr.	27	59	7	Yield contaminated with unknown.
13	50	14	170 C.	6 hr.	31	69	6	-
14	50	18	170 C.	6 hr.	35	78	0	Refined 2,4-dinitro-chlorbenzene used.

Table II. RESULTS OBTAINED IN THE PREPARATION OF NITROMETHANE

Run	Gms.	Gms.	Gms.	Gms. added	1st. distillation		2nd. distillation		3rd. distillation		Total c.c.	Gms.	% yield based on[1]		Remarks	Notes[2]
	$CH_2ClCOOH$	$NaNO_2$	NaOH	material	c.c. H_2O	c.c. CH_3NO_2	c.c. H_2O	c.c. CH_3NO_2	c.c. H_2O	c.c. CH_3NO_2	CH_3NO_2	CH_3NO_2	$NaNO_2$	$CH_2ClCOOH$		
1	100	60	43	-	225	10	92	19	29	4	33	33	50.5	41.5	-	a
2	100	60	43	-	230	10	100	19	30	4	33	33	50.5	41.5	-	a
3	100	60	43	-	270	10	150	21	60	9	40	36	55.1	46.1	-	b
4	100	60	43	1 gm. LiCl	265	10	140	21	38	5	36	34	52.0	42.8	-	a
5	100	60	43	1 gm. LiCl	260	10	100	20	35	5	35	32.5	49.8	41.0	-	b
6	100	60	43	60 gms. boric acid	275	1	120	21	36	4	26	25	38.4	31.4	-	a
7	100	60	45	60 gms. boric acid	500	1	200	26	104	10	37	35	53.7	44.1	Boric acid added to $CH_2ClCOOH$	a;c
8	100	60	45	60 gms. boric acid	400	4	120	23	34	6	33	32	49.0	40.3	Boric acid added to $CH_2ClCOOH$	b;c
9	100	60	43	60 gms. boric acid	400	0	110	25	35	8	33	32	49.0	40.3	Boric acid added to $CH_2ClCOONa$	a;c
10	100	60	43	60 gms. boric acid	445	1	103	25	40	6	32	31	47.4	39.1	Boric acid added to $CH_2ClCOONa$	b;c
11	100	60	43	332 gms. borax	240	7	90	18	30	4	29	28	42.9	35.2	-	a
12	100	60	43	332 gms. borax	270	9	92	18	35	4	31	30	46.0	37.8	-	b
13	100	60	43	37 gms. LiCl	254	12	93	18	32	5	35	33	50.5	41.5	-	b
14	100	60	--	-	250	9	92	20	33	5	34	32	49.0	40.3	Li_2CO_3 used for neutrallization	b
15	100	60	--	-	254	10	95	16	33	7	33	31	47.4	39.1	LiOH used for neutrallization	b
16	100	60	43	20 gms. soap	390	0	200	12	50	6	18	15	23.0	18.8	Foamed over on boiling	a
17	100	60	43	-	265	10	100	15	30	2	27	26	39.7	32.8	Run in CO_2 atmosphere	a
18	100	60	43	214 gms. $MgSO_4 \cdot 7H_2O$	270	16	95	15	20	2	33	33	50.5	41.5	-	b
19	100	60	43	60 gms. $(CH_2)_6N_4$	253	0	---	0	---	--	0	0	0	0	-	b
20	100	60	43	2.5 gms. gelatin	250	15	104	13	29	2	30	31	47.4	39.1	Foamed on heating	b
21	100	60	43	2 gms. $Be(NO_3)_2 \cdot 3H_2O$	280	11.5	98	18	25	3	32.5	33.5	51.4	42.1	Foamed and evolved NO_2 on heating	b
22	100	60	43	5 gms. casein	230	12	99	16	20	2	30	33	50.5	41.5	Foamed on heating	b
23	100	60	43	10 gms. Na_2SiO_3	253	12.5	110	17	20	2	31.5	33	50.5	41.5	Foamed on heating	b
24	100	60	43	1 gm. $Th(NO_3)_4$	263	10	92	20	28	2	32	34	52.0	42.8	NO_2 evolved cold; foam on heating	b
25	100	60	43	1.5 gms. $La(NH_4)_2(NO_3)_5 \cdot 5H_2O$	251	11	85	18	29	2	31	33	50.5	41.5	Foamed on heating	b
26	100	60	43	-	254	7	95	3	---	--	10	10	15.4	12.6	-	d
27	100	60	43	-	260	10	99	19	25	2	31	33	50.5	41.5	-	e
Mean													50.5	41.5	-	f

1. % yield is based on purified yield (0.812 X crude yield).

2. Key to notes given on page 19.

Key to Notes on Results

a. Sodium nitrite solution heated to boiling; sodium chloracetate then added slowly.

b. One quarter of the sodium chloracetate solution added before heating; the rest added slowly after boiling had started as in (a).

c. 250 c.c. water added.

d. Sodium chloracetate all added and the mixture refluxed for one hour before starting distillation.

e. Reaction run in a distilling flask.

f. Mean based on fourteen comparable runs.

SUMMARY

A study of certain conditions affecting the preparation of nitromethane has been made with a view to increasing the yield. A great variety of substances have been added as possible "catalysts", and although some brought about a decrease in yield, in no case was more nitromethane obtained than resulted from the standard procedure except in the presence of lithium salts where the yields were variable and not reproducible.

BIBLIOGRAPHY

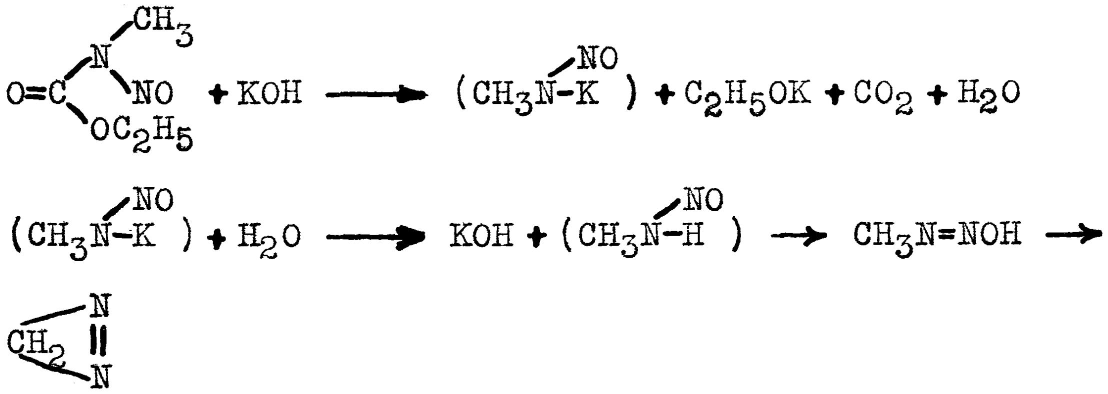
1. Kolbe, H., J. prak. Ch. (1) 5 429 (1872).
2. Meyer, V. and Stuber, Ber. 5 203;399 (1872).
3. Preibisch, R., J. prak. Ch. (2) 8 316 (1873).
4. Meyer, V., Ann. 171 32 (1874).
5. Auger, M. V., Bull. Soc. Chim. (3) 23 333 (1900).
6. Bamberger, E., Ber. 35 4300 (1903).
7. Walden, P., Ber. 40 3216 (1907).
8. Ray, P. C. and Neogi, P., Proc. Chem. Soc. 23 246 (1907).
9. Steinkopf, W., Ber. 41 4457 (1908).
10. Steinkopf, W. and Kirchoff, G., Ber. 42 3438 (1909).
11. Wahl, M. A., Bull. Soc. Chim. (4) 5 180 (1909).
12. Whitmore, F. C. and Whitmore, M. G., Organic Syntheses 3 83 (1923).
13. Alexieff and Carcanas, Bull. Soc. Chim. (4) 39 324 (1926).
14. Hirano, I., J. Pharm. Soc. Japan. 50 869 (1930).
15. Wang, A. B. and Tseng, C. L., C. Abs. 25 681 (1931). Nat'l. Cen. Univ. Sci. Rep'ts. Ser. A Phys. Sci. 1 27 (1930).
16. Pritzl, P. P. and Adkins, H., J. A. C. S. 53 234 (1931).

III.

The Preparation of Methyl Urea.

INTRODUCTION

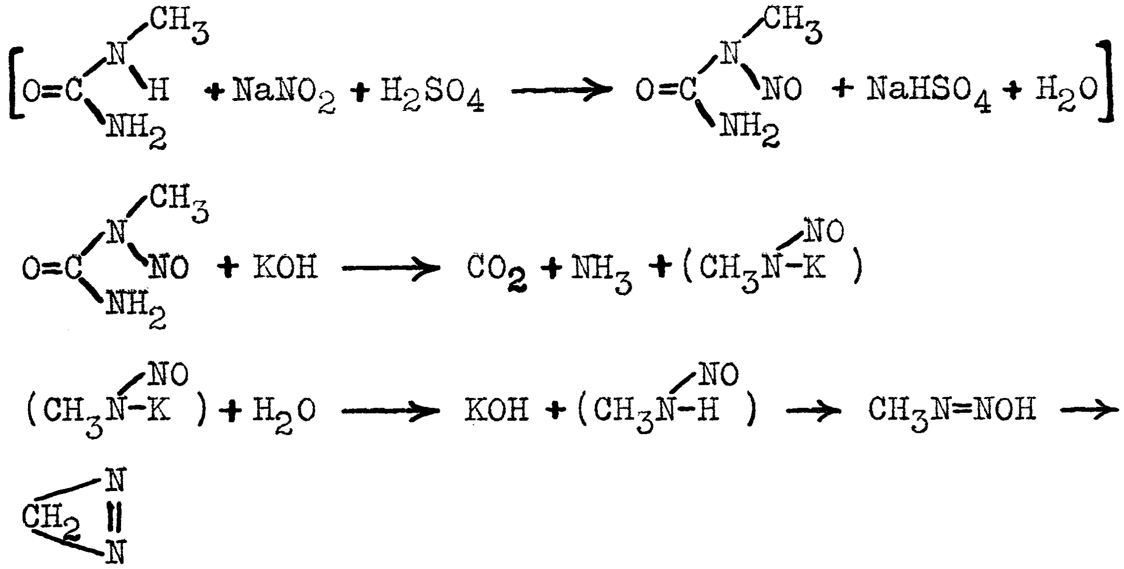
It is universally agreed that diazomethane is the most useful methylating agent known for general purposes. It has two drawbacks, however,- its toxicity and its difficulty of preparation; the former can be overcome by proper ventilation and care in manipulation. Diazomethane has usually been made by the action of alkaline solutions on nitrosomethylurethane:-



$$O{=}C\begin{matrix}\diagup N\begin{matrix}\diagup CH_3\\ \diagdown NO\end{matrix}\\ \diagdown OC_2H_5\end{matrix} + KOH \longrightarrow (CH_3\overset{NO}{N}\text{-}K) + C_2H_5OK + CO_2 + H_2O$$

$$(CH_3\overset{NO}{N}\text{-}K) + H_2O \longrightarrow KOH + (CH_3\overset{NO}{N}\text{-}H) \rightarrow CH_3N{=}NOH \rightarrow CH_2\begin{matrix}N\\ \|\\ N\end{matrix}$$

It can also be prepared from nitrosomethylurea:-



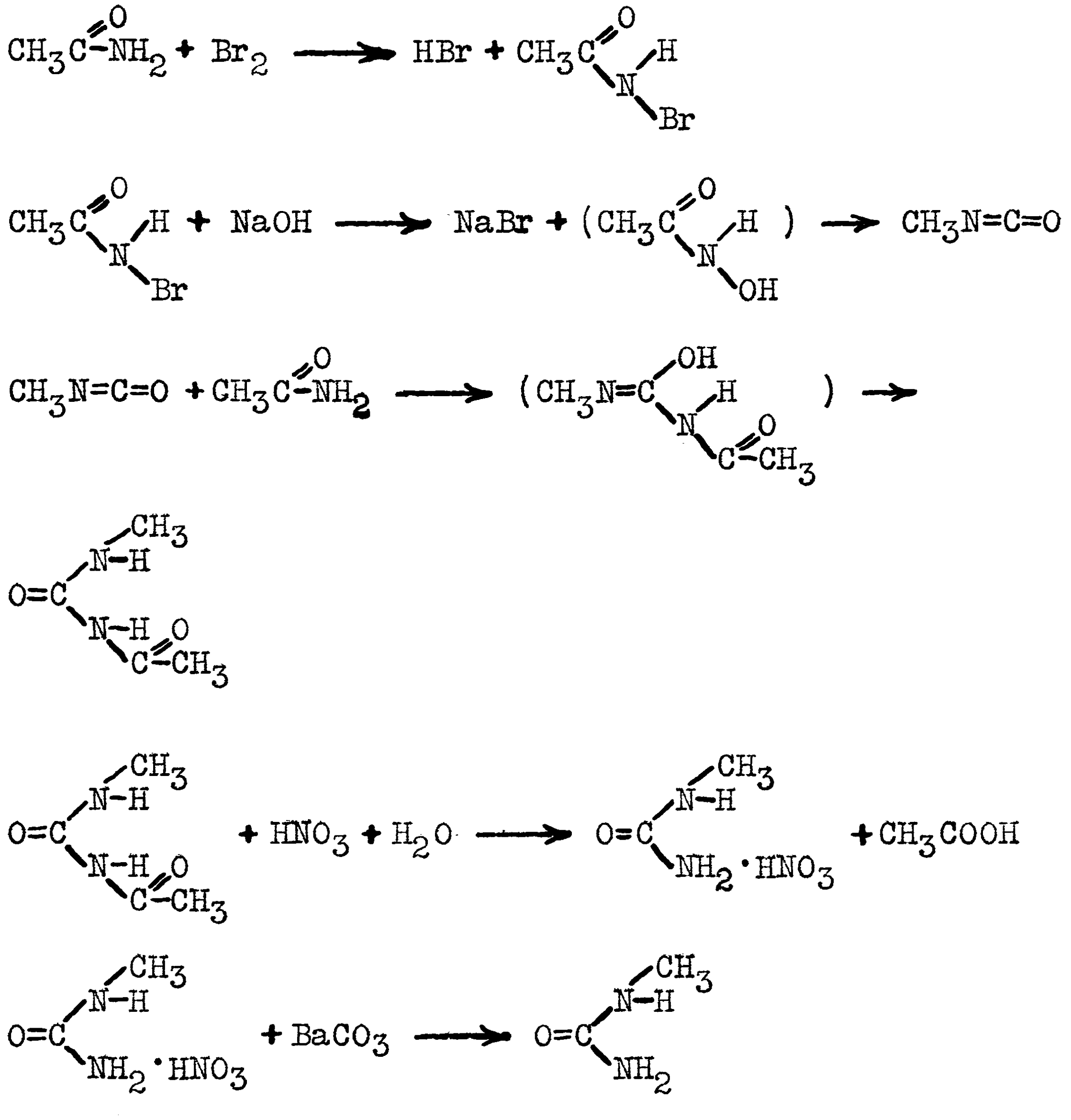
$$\left[O{=}C\begin{matrix}\diagup N\begin{matrix}\diagup CH_3\\ \diagdown H\end{matrix}\\ \diagdown NH_2\end{matrix} + NaNO_2 + H_2SO_4 \longrightarrow O{=}C\begin{matrix}\diagup N\begin{matrix}\diagup CH_3\\ \diagdown NO\end{matrix}\\ \diagdown NH_2\end{matrix} + NaHSO_4 + H_2O\right]$$

$$O{=}C\begin{matrix}\diagup N\begin{matrix}\diagup CH_3\\ \diagdown NO\end{matrix}\\ \diagdown NH_2\end{matrix} + KOH \longrightarrow CO_2 + NH_3 + (CH_3\overset{NO}{N}\text{-}K)$$

$$(CH_3\overset{NO}{N}\text{-}K) + H_2O \longrightarrow KOH + (CH_3\overset{NO}{N}\text{-}H) \rightarrow CH_3N{=}NOH \rightarrow CH_2\begin{matrix}N\\ \|\\ N\end{matrix}$$

Nitrosomethylurethane is relatively expensive to buy or make and is a liquid having disagreeable physiological properties. Nitrosomethylurea is an innocuous solid but is expensive owing to the price of methyl urea.

The purpose of this investigation was to devise a suitable method for the preparation of methyl urea. This looked like a relatively simple problem, for, according to Thorpe and Whitely[6], the original directions of Hofman[1] were satisfactory:-

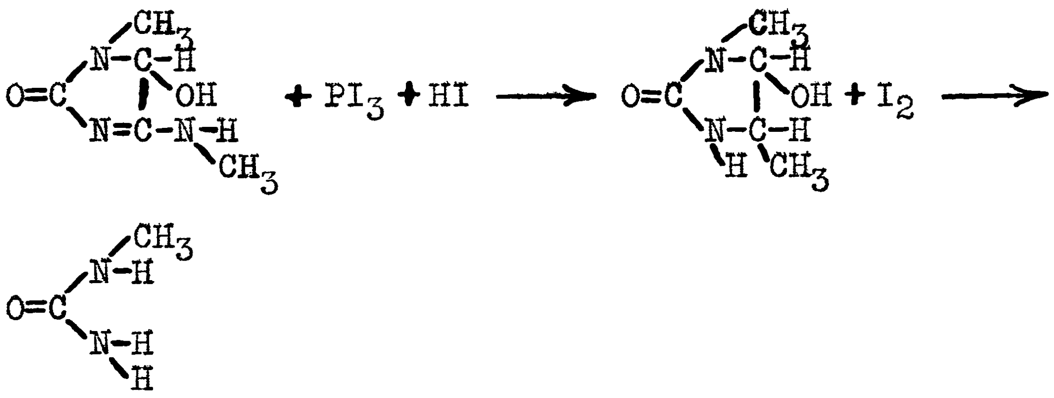


However, it turned out otherwise, and after considerable experimental work, the conclusion was reached that too many details of manipulation needed to be rediscovered before the process would be satisfactory. This same conclusion was reached by Arndt and Amende[7]. Since our copy of the journal containing their work was at the bindery, their article was not found in time to prevent our attempting to solve the problem. In their paper they give a most excellent discussion of the whole question and have included satisfactory experimental procedures for the preparation of the necessary intermediates, as well as solutions of diazomethane of known strength.

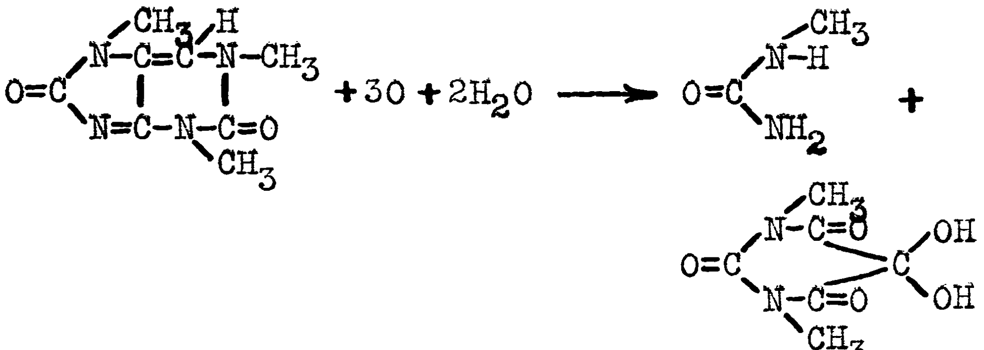
HISTORICAL

Hofman[1] made methyl urea as outlined by the equations on page 23.

Fischer[2] obtained methyl urea from caffoline as outlined by the equation:-



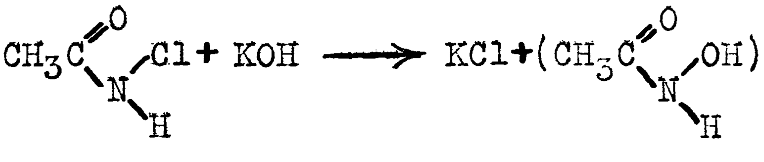
Fischer[3] also obtained methyl urea by treating caffeine with hydrochloric acid and potassium chloride according to the outline equation:-



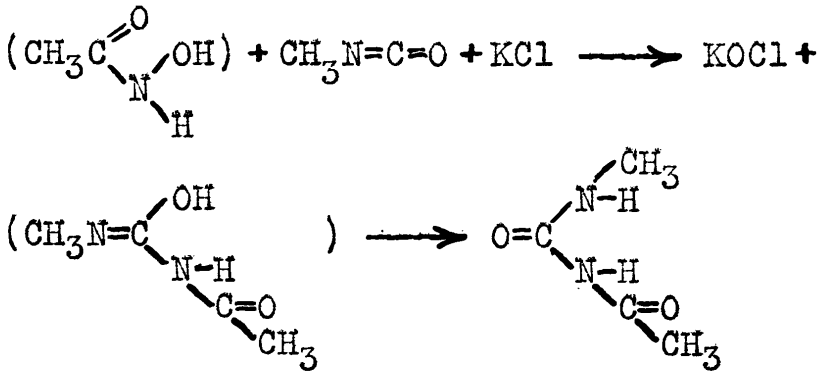
The by product is dimethyl alloxan.

Degner and Peckman[4] determined the melting point of methyl urea as 102°C.

Stieglitz and Earle[5] made acetyl methyl urea as outlined by the equation:-



$$CH_3C(=O)N(H)Cl + KOH \longrightarrow KCl + (CH_3C(=O)N(H)OH)$$



The melting point of the acetyl methyl urea thus obtained was 178.5° C.

Thorpe and Whitely[6] repeated the experiments of Hofman[1] with good results.

Arndt and Amende[7] found that the directions given by the previous workers were entirely inadequate in that too many experimental conditions have to be rediscovered.

EXPERIMENTAL

After studying the methods of preparation known for methyl urea, it was decided to follow those given by Thorpe and Whitely[6]. This procedure gave much lower yields than those claimed for acetyl methyl urea, and no methyl urea was obtained at all. Varying conditions affected the yield only slightly. The best yield obtained of acetyl methyl urea was less than 40%.

In the formation of methyl urea from the acetyl derivative, most of the nitrite was lost on washing, and the rest seemed to decompose during the reaction with barium carbonate.

According to directions, 10 grams of acetamide and 13.5 grams of bromine were mixed and cooled. 10% sodium hydroxide was added until the color turned yellow. The mixture was then heated on a steam bath and more sodium hydroxide solution added every time the color changed to red. Upon cooling, a 25% yield of acetyl methyl urea with a melting point of 181° - 182°C. was obtained. The process of heating on the steam bath took about one and one-half hours.

The conditions were varied greatly:-

a. Quantities of from one-half to double the theoretical amount of bromine required were used; the theoretical amount gave the best yield.

b. The full amount of bromine was added to one- half the full amount of acetamide and sodium hydroxide added to a yellow color. The other half of the acetamide was then added and the mixture heated as before. The same low yield was obtained.

c. The brominated product of acetamide was even isolated and let react with acetamide, but this did not increase the yield at all.

d. The reaction was tried in chloroform, toluene, and tertiary butyl alcohol as solvents, but no yield was obtained at all in these cases.

e. With larger quantities of reactants, the yields decreased rapidly; the reaction seems to favor small amounts of reactants.

f. The time of allowing the acetamide and bromine to set together before adding sodium hydroxide was increased up to 72 hours without any effect on the yield.

g. If all the sodium hydroxide were added at the same time instead of in small quantities as the red color appeared on heating, no red color appeared at all and no product was obtained.

Methyl urea nitrate was easily obtained from the acetyl methyl urea, but most of it was lost in washing, and no methyl urea resulted from heating this nitrate with barium carbonate. We had such a small amount of acetyl methyl urea that no further investigation was made of this preparation.

SUMMARY

Acetyl methyl urea can be obtained in poor yields from acetamide and bromine by the directions described.

BIBLIOGRAPHY

1. Hofman, A. W., Ber. 14 2725 (1881).

2. Fischer, E., Ber. 14 1908 (1881).

3. Fischer, E., Ann. 215 257 (1882).

4. Degner, O. and Peckman, H. V., Ber. 30 650 (1897).

5. Stieglitz, J. and Earle, R. B., J. A. C. S. 30 419 (1903).

6. Thorpe, J. F. and Whitely, M. A., A Students' Manual of Organic Chemical Analysis. page 136. Longmans, Green, and Co. (1925).

7. Arndt, F. and Amende, J., Zeit. angew. Ch. 43 444 (1930).

GENERAL SUMMARY

The experimental work described in this thesis has given the following results:-

1. Satisfactory reproducible directions for the preparation of 2,4-dinitraniline by two methods have been devised.

2. In the presence of lithium salts, the preparation of nitromethane from sodium chloracetate and sodium nitrite gives somewhat greater yields than the usual method originally devised by Steinkopf, but the difference is not great enough to warrant the increased cost.

3. The published directions for preparing methyl urea are unsatisfactory in spite of their claims. This conclusion has been independently reached by workers in Germany.
The first step, acetyl methyl urea, gives yields of less than 40%; we were unable to increase this yield.