along the length of the cellulose macromolecules, the maximum frequency of completely unsubstituted glycol units was calculated to be $H^2/4$. When alkylation was localized in intermittent lengths of the cellulose chain, the probable frequency of glycol units was $H/2$. The actual occurrence was determined by oxidation with sodium periodate.

3. Alkylation of cellulose dispersed in a quaternary ammonium base gave a water soluble product with a glycol content close to $H^2/4$ while the technical, heterogeneous alkylation of alkali cellulose to the same degree (substitution 0.6) resulted in water insoluble products with a glycol count of $H/2$. The other characteristics of the two products were so similar that the insolubility of the latter in water could only be connected with the highly non-uniform substitution of the macromolecules. All the data gave very strong support to the views of Lorand and Georgi [THIS JOURNAL, **59,** 1166 (1937)] on the mechanism of the alkylation of alkali cellulose, and to those of Bock [*Ind. Eng. Chem.*, **29,** 985 (1937)] on the type of distribution required for solubility in water.

4. In a homogeneous medium, the primary hydroxyl groups in cellulose were alkylated approximately as fast as both secondary groups together. This ratio was smaller in heterogeneous alkylations and was less than the calculated minimum for water soluble products prepared in this way. The inference was that the primary hydroxyl groups were partially shielded from the reagent at this stage of the alkylation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

The Direct Diazotization of Nitrobenzene

BY F. W. BERGSTROM AND J. S. BUEHLER

In 1904, Bamberger and Wetter[1] observed that a very small amount of benzene-1-azo-naphthol-2 (0.38 g. from 20 g. nitrobenzene) was formed when a petroleum ether solution of nitrobenzene and 2-naphthol were shaken in the cold for several days with finely powdered sodium amide. In an attempt to prepare *o*- and *p*-nitroaniline, Bradley and Robinson[2] allowed sodium amide to stand with nitrobenzene (1.3 moles) in an enamelled steel cylinder for six months. One of the substances isolated in small yield corresponded in composition to a nitrohydroxyphenazine. Williams[3] found that benzene-1-azo-naphthol-2 was formed in fair yield by adding nitrobenzene to a solution of 2-naphthol in an excess of potassium amide dissolved in liquid ammonia. It is with this reaction that the present paper is concerned.

Nitrobenzene reacts with an excess of sodium amide or potassium amide in liquid ammonia at −33° or at room temperatures to give a deep reddish-brown solution from which an apparently dark colored precipitate slowly deposits. Nitrogen is evolved at both temperatures, very roughly in the ratio of one mole per two moles of nitrobenzene. Such ammonia solutions when evaporated to dryness leave an explosive residue that is rather sensitive to shock. Hydrolysis of the reaction product before the evaporation of the liquid ammonia gives an oil from which nothing has been obtained. Similarly, little or nothing of definite characteristics was obtained by the reaction of excess potassium amide with a number of other nitro compounds.

If nitrobenzene is added to a solution of 2-naphthol in an excess of alkali amide in liquid ammonia, benzene-1-azo-naphthol-2 is formed in yields up to about 30% of the theoretical, with the simultaneous evolution of nitrogen. When sodium amide and nitrobenzene are allowed to react in liquid ammonia at −33° until formation of nitrogen has practically ceased, and 2-naphthol is then added, approximately the same yield of dye is obtained. The diazo compound responsible for dye formation is thus either produced with evolution of nitrogen, or the latter gas arises from an independent reaction. The optimum yields of dye result when about six moles of amide are used per mole of nitrobenzene.

Since sodium benzeneisodiazotate does not react with sodium amide and 2-naphthol under the conditions of these experiments, it is obvious that normal benzenediazoic acid or its sodium salt is

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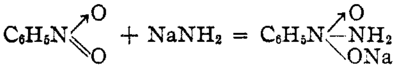
[1] Bamberger and Wetter, *Ber.*, **37,** 629 (1904).

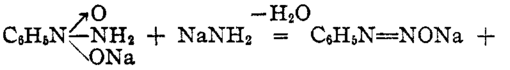
[2] Bradley and Robinson, *J. Chem. Soc.*, 1262 (1932).

[3] Williams, unpublished work, Stanford University, 1930.

the true intermediate in the production of benzene-1-azo-naphthol-2. The following partial mechanism is suggested tentatively.



$$C_6H_5N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} + NaNH_2 = C_6H_5N\begin{smallmatrix}\nearrow O\\ \leftarrow NH_2\\ \diagdown ONa\end{smallmatrix} \qquad (1)$$



$$C_6H_5N\begin{smallmatrix}\nearrow O\\ \leftarrow NH_2\\ \diagdown ONa\end{smallmatrix} + NaNH_2 \overset{-H_2O}{=} C_6H_5N{=}NONa + NaOH + NH_3 \qquad (2)$$

The equation for dye formation is therefore

$$C_6H_5NO_2 + 3NaNH_2 + C_{10}H_7OH = C_6H_5N{=}NC_{10}H_6ONa + 2NaOH + 2NH_3 \qquad (3)$$

since the phenolic hydroxyl is certainly acidic in ammonia.

The addition compound of equation (1), possibly in its tautomeric form $\left[C_6H_5N\begin{smallmatrix}\nearrow OH\\ \rightarrow NH\\ \diagdown O^-\end{smallmatrix}\right]Na^+$, might lose hydroxyl ion to give the mixed aquo ammono nitrobenzene, $C_6H_5N\begin{smallmatrix}\nearrow O\\ =NH\end{smallmatrix}$, which Angeli believes to represent normal benzenediazoic acid.[4] If Angeli's view is incorrect, one could still assume the intermediate formation of the aquo ammono nitrobenzene, which rearranges to a benzene normal diazoic acid of the conventional formula $C_6H_5N{=}N{-}OH$.

The formation of colored material (red or orange-red, and probably a dye) was observed when excess sodium amide and 2-naphthol reacted with the following in liquid ammonia at −33°: *p*-nitrotoluene, *o*-nitrotoluene, *o*-nitrobenzoic acid, *p*-nitrobenzoic acid, *p*-nitrodiphenyl and *p,p'*-dinitrodiphenyl. In no case was it possible to separate pure compounds. *p*-Nitrodimethylaniline, *p*-nitroanisole, 1-nitronaphthalene and ω-nitrostyrene either formed no dye at all, or at the most only a trace. The largest quantities of reddish solid apparently were formed in the reactions involving the nitrotoluenes. It will be noted that all of the nitro compounds with one exception are *o*- and *p*-derivatives of benzene, and there may often be some interaction between the two groups. Thus, Erickson[5] has obtained some evidence for the formation of a sodium salt of *o*-nitrotoluene, $NaCH_2C_6H_4NO_2$, whose existence could be predicted on the basis of the principle of vinylogy.[6]

Experimental

The Action of the Alkali Amides on Nitrobenzene.—An excess of both sodium amide and potassium amide reacts readily with nitrobenzene at −33° or at room temperature to give opaque-brown or reddish-brown solutions, with the formation of a precipitate and the evolution of nitrogen. If ammonia is evaporated from the reaction mixture, the dry residue is found to be explosive and rather sensitive to shock. Addition of an ammonium salt or of water in excess to the liquid ammonia solution will inactivate the substances responsible for the explosion.

In a two-legged sealed glass tube[7] the potassium amide from 10.23 milliatoms of potassium was slowly poured into a solution of 10.00 millimoles of nitrobenzene. Gases, collected after three days at room temperature, consisted of 132 cc. of nitrogen (standard conditions; 5.90 millimoles, or 0.59 mole nitrogen per mole of nitrobenzene). In a repetition (potassium amide from 0.5 g. of potassium, 0.6 g. of nitrobenzene; reaction tube provided with a glass stopcock) 51 cc. of nitrogen under standard conditions was collected, or 0.5 mole per mole of nitrobenzene. The gas was collected over a period of three hours, but two-thirds was given off during the first five minutes.

Calcium amide, which is almost insoluble in liquid ammonia, reacts slowly with nitrobenzene at room temperatures with evolution of nitrogen, but only tar is formed.

The Action of the Alkali Amides on Other Nitro Compounds.—1-Nitronaphthalene, *o*-nitroaniline, *m*-dinitrobenzene, *o*-nitrophenol + KNO_3, and 6-nitroquinoline + KNO_3 react with an excess of alkali amide with evolution of nitrogen and the formation of oils, tars or blackish materials that decompose at a high temperature. In the case of 1-nitronaphthalene, there was evidence for the formation of a very small amount of a definite product.

The Action of Amides on Nitrobenzene in the Presence of 2-Naphthol.—The experiments listed in Table I were carried out in the following general manner: a 500-cc. round-bottom flask was about half filled with liquid ammonia at its normal boiling point. A small amount (0.1 g. or less) of hydrated ferric nitrate was added and this was followed after a few minutes by a small piece of sodium (0.1 g.) to reduce the nitrate to metallic iron. The quantity of sodium given in the table was then introduced. When sodium amide had been formed (gray precipitate), 2-naphthol was added, and nitrobenzene then run in dropwise from a dropping funnel. The reaction appeared to be complete within a few minutes, but the flask was nevertheless allowed to stand for one hour, and then an excess (1.5 moles per atom of sodium) of ammonium chloride added to destroy reactive sodium salts. After evaporation of the remaining ammonia, water was introduced and the copious red precipitate collected on a filter, washed with dilute sodium hydroxide to remove 2-naphthol and inorganic material, and then crystallized from alcohol (iron was filtered from the hot solution). The melting point of the twice crystallized material was 133.0°, cor.; the mixed melting point with authentic benzene-1-azo-naphthol-2 was the same, showing their identity. Yields given in Table I are of the once crystallized product.

Gases Formed in the Reaction of Sodium Amide on Nitrobenzene in the Presence of 2-Naphthol.—The following reactions were carried out at −33° in a vessel similar to one previously described[8] except that the top was closed

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[4] Angeli, *Ber.*, **59**, 1400 (1926); **62**, 1924 (1929); *Gazz. chim. ital.*, **51**, 35–42 (1921); Cambi and Szego, *Ber.*, **61**, 2081 (1928).

[5] Erickson, Thesis, Stanford University, 1940.

[6] Fuson, *Chem. Reviews*, **16**, 12 (1935).

[7] Bergstrom, THIS JOURNAL, **56**, 1749 (1934).

[8] Bergstrom, *Z. anorg. Chem.*, **221**, 118 (1934).

TABLE I

10 millimoles of nitrobenzene was used in each reaction.

No.	Amide, millimoles	2-Naphthol, millimoles	Yield of dye, g. (%)
1	$NaNH_2$, 31	11	0.329 (13)
2	$NaNH_2$, 35	11	.661 (27)
3	$NaNH_2$, 45	11	.602 (25)
4	$NaNH_2$, 60	11	.823 (33)
5	$NaNH_2$, 35	15	.498 (20)
6	$NaNH_2$, 40	15	.616 (25)
7	$NaNH_2$, 50	15	.648 (26)
8	$NaNH_2$, 65	15	.703 (29)
9	KNH_2, 60	11	.602 (25)
10[a]	$NaNH_2$, 61	11	.746 (30)
11[b]	$NaNH_2$, 61	11	.582 (24)

[a] Mixture hydrolyzed after one hour with water instead of with ammonium chloride. [b] Nitrobenzene was added to the sodium amide, and after one hour excess amide was destroyed with ammonium chloride (5 g.). 2-Naphthol was then introduced. About the same yield of dye was obtained if water was used to destroy excess amide instead of ammonium chloride.

with a short buret whose tip was sealed through the ground glass stopper. The top of the buret was attached by rubber tubing to a source of low ammonia pressure for forcing the contents into the liquid ammonia solution contained in the reaction vessel.

Sodium amide was made in ammonia from 2.0 g. sodium with the use of 0.05 g. of ferric nitrate as catalyst, and 4 g. of 2-naphthol was then introduced. All water insoluble gases were swept into a large nitrometer[9] and then 2.05 cc. of nitrobenzene was added slowly from the buret. There was collected in the nitrometer 93.4 cc. gas, standard conditions, consisting of 7.7% hydrogen and 92.3% nitrogen.

The above experiment was repeated, with these differences: nitrobenzene (2.46 g. in 4 cc. of benzene) was added to the sodium amide suspension in ammonia and gases resulting from this reaction were collected. 2-Naphthol (4 g.) was then introduced from the side tube; very little additional gas was formed (total volume 94.3 cc., standard conditions, 4% hydrogen, remainder nitrogen). The origin of the hydrogen is unknown. No nitrous oxide could be detected in either experiment (slow combustion of gases with hydrogen). The yield of benzene-1-azo-naphthol-2 was 25%.

Sodium Benzeneisodiazotate.—Sodium benzeneisodiazotate (1.6 g., 0.01 mole) was added to a liquid ammonia suspension of the sodium amide prepared from 1.0 g. (43 milliatoms) of sodium. 2-Naphthol (1.6 g., 11 millimoles) was then introduced, but no color developed. The excess sodium amide was destroyed by ammonium chloride, and then, after evaporation of the ammonia, water was added. Dye slowly formed during the next few days, as would be expected from the behavior of sodium benzeneisodiazotate in mildly alkaline (ammonia) solution.

Acids in water convert potassium benzeneisodiazotate to the normal diazonium salt, but ammonium bromide, an acid in liquid ammonia, does not cause this change. Potassium benzenediazotate (1.6 g.) in liquid ammonia was treated with 1.5 g. of ammonium bromide; after one hour, there was siphoned into this a liquid ammonia solution of 1.6 g. of 2-naphthol in the potassium amide from 1.5 g. of potassium (prepared with the use of an iron oxide catalyst). There was no reddening of the solution or precipitation of dye.

Summary

1. Sodium amide and potassium amide in excess react with nitrobenzene with evolution of nitrogen and the formation (after hydrolysis of the reaction mixture) of an oil from which no definite compounds have been isolated. Calcium amide converts nitrobenzene at room temperatures to a tar with evolution of nitrogen.

2. Sodium amide and potassium amide in excess react with nitrobenzene and 2-naphthol in liquid ammonia to give benzene-1-azo-naphthol-2 in yields up to about 30% of the theoretical. Nitrogen is evolved at the same time, possibly as a result of an independent reaction.

3. Sodium (or potassium) benzene normal diazotate is very probably the intermediate in the reaction; when formed it persists for some time in liquid ammonia. Sodium benzeneisodiazotate does not couple with 2-naphthol in liquid ammonia in the presence of sodium amide.

4. Many other nitro compounds react with the alkali amides in the presence of 2-naphthol to form red or reddish-brown solutions, or precipitates, but no definite compounds have been crystallized from the rather complex mixtures.

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[9] *Cf.* Fernelius and Bergstrom, *J. Phys. Chem.*, **35**, 742 (1931), J, K, L, M, N of Fig. 1.