was hydrogenated under pressure at 70–80°; the resulting product, which reacted mildly with a nitrating mixture, was treated with 15% fuming sulfuric acid in order to remove any traces of olefins. The hydrogenated product after purification distilled at 163–165°; m. p. −18°, $n^{20}D$ 1.4577; $d^{20}_4$ 0.8613.

*Anal.* Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.87; H, 12.77.

This compound corresponds to isobornylane.

## Summary

Terpineol, 1,8-*p*-menthanediol, dihydroterpineol, menthol, borneol and isoborneol were dehydrated under pressure in the presence of dilute aqueous solutions of magnesium chloride at temperatures ranging from 230 to 320°.

Terpineol and 1,8-*p*-menthanediol on dehydration yielded dipentene, α-terpinene, and small amounts of an unknown terpene, which formed a characteristic solid tetrabromide.

4-Methyl-1-isopropyl-1-cyclohexene was obtained from the dehydration of dihydroterpineol.

Menthol on dehydration formed a compound corresponding to 2-methyl-5-isopropyl-1-cyclohexene.

Isoborneol dehydrated to camphene, while borneol formed a mixture consisting of camphene and a liquid isomer of camphene.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# Direct Aromatic Amination: A New Reaction of Hydroxylamine-O-sulfonic Acid[1]

BY R. N. KELLER AND PETER A. S. SMITH

## Introduction

In 1924 Karl Schmidt[2] converted benzene directly to aniline, and carbonyl compounds to substituted amides, by reaction with hydrazoic acid in the presence of sulfuric acid. Sommer, Schulz and Nassau[3] aminated primary amines to hydrazines by means of hydroxylamine-O-sulfonic acid ($H_2N$-O-$SO_3H$).[4] In both instances these reactions were explained on the basis of the intermediate formation of the radical NH. Specht, Browne and Sherk[6] have shown the close relationship between the two aminating agents by preparing hydroxylamine-O-sulfonic acid from hydrazoic acid and fuming sulfuric acid. They explained this on the basis of the intermediate formation of $NH_2^+$. Since NH can be expected to have a proton affinity, and Schmidt's reaction took place under strongly acid conditions, it appears preferable to formulate his intermediate as $NH_2^+$ also. The reaction of Sommer, Schulz and Nassau takes place in alkaline solution, and NH as such may actually be the intermediate.

The work of Schmidt prompted the investigation of the mechanism of the decomposition of hydrazoic acid.[7,8,9] The decomposition was found to be unimolecular, and could best be explained by assuming that $HN_3 = N_2 + NH$ is the rate-determining step. Gleu,[7] using ultraviolet light to decompose aqueous hydrazoic acid, found one-third of the nitrogen in solution as hydroxylamine, which is very similar to the finding of Schmidt that the decomposition of hydrazoic acid by sulfuric acid also yields hydroxylamine.

Tolmachev[10] has identified the bands of NH in the spectra obtained by exploding hydrazoic acid.

The assumption that NH or $NH_2^+$ is the intermediate in all these reactions leads to the expectation that the amination of aromatic nuclei would be accomplished by reaction with hydroxylamine-O-sulfonic acid, and with hydrazoic acid under the action of ultraviolet light. Our experiments have confirmed this expectation.

## Experimental[11]

Hydroxylamine-O-sulfonic acid was prepared according to Sommer, Schulz and Nassau[3] from redistilled chlorosulfonic acid and hydroxylammonium sulfate. Most of the aminations were run with the material thus obtained without further purification; in a few cases, purified[3] HSA[4] was used, but the increase in yield was a few per cent. at most. All other chemicals were of reagent quality or the equivalent.

HSA by itself is stable toward aromatic hydrocarbons. This is to be expected if its reactivity is due to the formation of NH, because the pure acid does not decompose below its melting point, 210°. A mixture of the acid with

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[1] From the Doctoral dissertation of Peter A. S. Smith.

[2] K. F. Schmidt, *Ber.*, **57**, 704 (1924).

[3] F. Sommer, O. F. Schulz and M. Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925).

[4] The compound $H_2NOSO_3H$ has been referred to in *Chemical Abstracts* by no less than five different names, often without cross reference. No single name seems to have been accepted by more than one author. We propose to use the name "hydroxylamine-O-sulfonic acid,"[5] which we consider more appropriate than names containing the prefix "per." It also conforms to the current *Chemical Abstracts'* nomenclature for hydroxylamine derivatives (*cf.* the well-known "hydroxylamine-N-sulfonic acid," $HSO_3$-NH-OH). In some places in this paper the abbreviation HSA will be used.

[5] *Cf.* P. Baumgarten and H. Erbe, *Ber.*, **71**, 2603 (1938).

[6] H. E. M. Specht, A. W. Browne and K. W. Sherk, THIS JOURNAL, **61**, 1083 (1939).

[7] K. Gleu, *Ber.*, **61**, 702 (1928).

[8] A. O. Beckmann and R. G. Dickinson, THIS JOURNAL, **52**, 124 (1930).

[9] R. Meyer and H. J. Schumacher, *Z. physik. Chem.*, **A170**, 33 (1934).

[10] Y. M. Tolmachev, *J. Phys. Chem.* (U. S. S. R.), **14**, 615 (1940).

[11] All temperatures given for melting points are corrected.

anhydrous aluminum chloride liberates hydrogen chloride and brings about amination of aromatic compounds at temperatures above 60°. The most satisfactory results were obtained using about two moles of aluminum chloride to one of HSA, and an excess of the aromatic compound. Substances other than aluminum chloride were tried, but showed little or no activity. The following example (1) typifies the general procedure employed.

(1) **Amination of Toluene with HSA.**—Toluene (10 ml.), HSA (1.13 g.), and aluminum chloride (2.5 g.) were heated together for half an hour with motor stirring at 95–105°. The mixture was allowed to cool, and a slush of ice and dilute hydrochloric acid added; the separated aqueous phase was extracted with ether to remove non-basic organic material, leaving a clear, colorless solution. Sufficient 20–30% sodium hydroxide was added to dissolve the aluminum hydroxide, and the solution was again extracted with ether. Evaporation of the dried extracts left 0.410 g. of yellow, oily toluidines. The yield[12] of the crude product on the basis of the aminating agent was 40%.

The oil was converted into an acetyl derivative of melting point 145–148° in 96% yield; this was accomplished by precipitating *p*-toluidinium oxalate from ether,[13] and acetylating with acetic anhydride. The ethereal filtrate, which should have contained any *o*-toluidine, yielded no crystalline material on acetylation. Recrystallization of the crude acetyl derivative gave white needles, m. p. 148–150°; mixed m. p. with acet-*p*-toluidide, 148–150°; ebullioscopic molecular weight in benzene, found 150, calculated for acet-*p*-toluidide 151.

The amination of toluene was run several times, with yields varying from 30 to 51%, seeming to depend on the physical condition of the HSA and on the efficiency of mixing. In the cases tested, unreacted HSA was detected among the reaction products by its oxidizing action on iodide ion. Unreacted toluene, used in excess, was always present.

(2) **Amination of Other Aromatic Compounds.**—Under similar treatment, a 28% yield of aniline was obtained from benzene, calculated on the basis of HSA used. This was converted to acetanilide, m. p. 104–107°, mixed m. p. 111–113°; ebullioscopic molecular weight in benzene, found 139, calculated 135. This was brominated in chloroform, yielding white crystals, m. p. 164.5–166.5° (m. p. of *p*-bromo-acetanilide 166–167°). Results shown in the table were similarly obtained.

OTHER COMPOUNDS AMINATED BY HSA AND PRODUCTS OBTAINED

| Compound aminated | Yield calcd. from HSA,[12] % | M. p. of acetyl deriv., °C. | Melting points of known compounds, °C. | |
|---|---|---|---|---|
| *o*-Xylene | 21 | 105–123 | 3,4-Di-Me-acetanilide | 99 |
| | | | 2,3-Di-Me-acetanilide | 132 |
| *m*-Xylene | 16 | 126.5–127.5 | 2,4-Di-Me-acetanilide | 128–129 |
| *p*-Xylene | 13 | 138–139 | Acet-*p*-xylidide | 138–139 |
| Chlorobenzene | 2.3 | 162–170 | *o*-Chloroaniline | 88 |
| | | | *m*-Chloroaniline | 72.5 |
| | | | *p*-Chloroaniline | 175–177 |
| Nitrobenzene | *ca.* 1 | 150–154 | *m*-Nitroacetanilide | 154 |

Anisole yielded a small amount of amine detectable by diazotization and coupling with β-naphthol, but too small for further identification. Some aminophenol appeared to have been formed as well, from cleavage by the aluminum chloride.

(3) **Decomposition of Hydrazoic Acid in Toluene by Ultraviolet Light.**—A concentrated, acidified solution of 1 g. of sodium azide was extracted with 40 ml. of toluene. The toluene solution, after drying over sodium sulfate, was irradiated for two hours by a 40-watt mercury arc ultraviolet lamp, while kept at 15 ± 2°. The solution slowly turned golden, and a brown rime collected on the walls of the containing vessel; there was only a barely perceptible evolution of gas. After irradiation, the toluene was extracted with dilute hydrochloric acid, and the acid solution was diazotized and coupled with β-naphthol. A bright orange-red precipitate of azo-dye showed the presence of toluidine. The amount was very small due to the low energy output of the ultraviolet lamp used.

As a control, a solution of hydrazoic acid in toluene was allowed to stand in the dark for twelve hours. The solution remained completely colorless, and contained no amine detectable by diazotization.

(4) **Amination of Toluene by Schmidt's Reaction.**—To a toluene solution of hydrazoic acid, prepared as described in (3), aluminum chloride (3 g.) was added in small portions. After standing for twelve hours at room temperature, with occasional stirring, the reaction mixture was worked up by the procedure described in (1). There was produced 0.26 g. of yellow oil, which was separated into the isomeric toluidines by ethereal oxalic acid, as in (1). Acetylation of the two fractions yielded 0.235 g. of white needles, m. p. 143–144° without further purification (m. p. acet-*p*-toluidide, 153°), and 0.065 g. of white needles, m. p. 104–105° (m. p. acet-*o*-toluidide, 110°; acet-*m*-toluidide, 65°).

(5) **Amination of Nitrobenzene with Hydrazoic Acid.**—When nitrobenzene was subjected to the procedures described in (3) and in (4), the formation of some amine was detectable by diazotization and coupling with β-naphthol, but the quantity was not sufficient for further identification. The substitution of concentrated sulfuric acid for aluminum chloride in procedure (4) did not give a better result. Much dark-colored, neutral material was always produced.

(6) **Reaction of Aluminum Chloride on Hydrazoic Acid Solutions.**—Solutions of hydrazoic acid in *sym*-tetrachloroethane, and in petroleum ether (b. p. 90–100°), were prepared as described in (3) and dried over sodium sulfate. The addition at room temperature of finely-divided, anhydrous aluminum chloride to each caused a vigorous evolution of gas. When the reactions appeared to be over, the mixtures were extracted with cold water, and tested with Nessler reagent and with chlorauric acid. This showed the presence of much ammonia in the extract from the tetrachloroethane, and hydrazine in that from the petroleum ether. The presence of these products can be explained on the basis of the initial reaction $HN_3 = NH + N_2$, brought about by the aluminum chloride.[14]

Since the aminations by HSA are not reversible, the fact that they do not go to completion is best accounted for by mechanical coating of the insoluble reactants by the insoluble products. This is to be expected from the gummy nature of the reaction mixture. The relatively low yields obtained are about the same as those reported by Schmidt,[15] both with respect to hydrocarbon and aminating agent, and leave much to be desired for synthetic purposes. The high melting point of HSA, 210°, and its insolubility in non-polar solvents suggest that it is a zwitterion of the structure $^{+}H_3N—O—SO_3^{-}$, like that which

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[12] Yields are calculated assuming that all the HSA used is a potential source of NH according to $H_2NOSO_3H \rightarrow NH + H_2SO_4$.

[13] C. Graebe, *Ber.*, **34**, 1778 (1901).

[14] For a review of the suggested modes of decomposition of NH, in the presence and absence of hydrazoic acid, see Gmelin-Kraut, "Handbuch der anorganischen Chemie," 8th ed., Vol. IV, 1936, p. 306.

[15] K. F. Schmidt, *Friedl., Fort. Teerfarb.*, **15**, 221 (1926).

has been proposed for sulfamic acid and trimethylamine–sulfur trioxide.[5,16] This suggests the desirability of preparing derivatives which would be more soluble in non-polar solvents. Preliminary results have already indicated that the ethyl ester of HSA is an aminating agent; other O-substituted hydroxylamines and the salts of HSA are also being investigated.

## Discussion

The original explanation of Schmidt that the aminations of carbonyl compounds and of aromatic nuclei by hydrazoic acid proceed through the radical NH has been the subject of much discussion.[17–22] It has not been made entirely clear whether NH, $NH_2^+$, $HN_3$, or $H_2NOSO_3H$ is the active agent, nor even whether amination of the two classes of compounds proceeds by the same mechanism. It has been claimed that the entire $HN_3$ molecule attacks, and sound experimental evidence has been put forth in support of this idea;[20,22] however, these experiments were concerned entirely with the reaction between carbonyl compounds and hydrazoic acid. We shall try to show that this reaction must proceed through a mechanism different from that of the reaction between aromatic nuclei and hydrazoic acid, and that the mechanism of the latter is essentially that first proposed by Schmidt, and modified by Specht, Browne and Sherk.

Further support for this lies in the following. Cationoid attacking agents obey the customary orientation rules, while anionoid attacking agents are directed exactly oppositely, and attack by them is hindered by so-called ortho–para-directing groups, and facilitated by so-called meta-directing groups. The aminations of aromatic nuclei by hydrazoic acid and by HSA obey the usual orientation rules, and they therefore must proceed through a cationoid mechanism. This suggests that $NH_2^+$ may be the attacking agent; however, NH might also show cationoid behavior, since, being isoelectronic[23] with atomic oxygen, it can be expected to have a pronounced electron affinity. It is interesting to compare the behavior of this radical with that of phenyl free radicals, which Grieve and Hey[24] have shown to attack mono-substituted benzenes in the ortho and para positions, independent of the group already on the ring. They attributed this to the nearly equal ability of the phenyl radical to accept or donate an electron.

We have found that aniline is not produced when benzene is heated at 60° with HSA and concentrated sulfuric acid, the conditions under which Schmidt obtained aniline from hydrazoic acid. Therefore, HSA cannot be an intermediate in Schmidt's reaction.

Our conclusion that the aminations of aromatic nuclei proceed through the radical NH (or perhaps $NH_2^+$) is therefore based on the following observations:

A. Carbonyl compounds are attacked very readily by hydrazoic acid, most of them under conditions where the latter is otherwise quite stable; aromatic nuclei, on the other hand, are aminated only with difficulty, and only under conditions such that the decomposition of hydrazoic acid is proceeding actively.

B. We have now shown that NH by itself, when generated photo-chemically from hydrazoic acid, is capable of aminating toluene.

C. The amination of aromatic nuclei is always accompanied by the formation of one or more of the decomposition products of NH, namely: $NH_3$, $N_2H_4$, $NH_2OH$.

D. The aminations of aromatic nuclei have been shown to be cationoid in character (anionoid attack has been suggested by Hurd[19]).

E. The whole evidence supports the assumption that the aminations by HSA and by hydrazoic acid take place by the same mechanism, and this can be reasonably explained only by assuming NH or $NH_2^+$ as a common intermediate.

It is possible that the small amounts of amines obtained by Graebe[13] from aromatic hydrocarbons and hydroxylammonium chloride in the presence of aluminum chloride may have arisen by a mechanism similar to that discussed above.

## Summary

1. Benzene and seven other aromatic compounds have been aminated by reaction with hydroxylamine-O-sulfonic acid ($H_2N$-O-$SO_3H$) in the presence of aluminum chloride.

2. Toluene has been aminated in small yield by hydrazoic acid under the action of ultraviolet light.

3. These new reactions, as well as aminations of aromatic compounds by hydrazoic acid in the presence of chemical catalysts, have been concluded to have as a common intermediate NH or $NH_2^+$.

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(16) P. Baumgarten, *Ber.*, **62**, 820 (1929).

(17) E. Oliveri-Mandalà, *Gazz. chim. ital.*, **55**, 271 (1925).

(18) K. F. Schmidt, *Ber.*, **58**, 2413 (1925).

(19) C. D. Hurd, in Gilman "Organic Chemistry," 1st ed., Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 698.

(20) M. A. Spielman and F. L. Austin, This Journal, **59**, 2658 (1937).

(21) T. Curtius and A. Bertho, *Ber.*, **59**, 565 (1926); A. Bertho, *ibid.*, **59**, 589 (1926).

(22) L. H. Briggs and J. W. Lyttleton, *J. Chem. Soc.*, 421 (1943).

(23) H. G. Grimm, *Z. Elektrochem.*, **31**, 474 (1925).

(24) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).