The Sulphonation of N-Ethyl Benzyl Aniline

by

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ABSTRACT

A slight modification of the existing plant procedure at the Fred'k. H. Levey Co. is described whereby greater and more consistent yields of ethyl benzyl aniline meta-sulfonic acid may be obtained.

Proof is presented that the sulfonic acid group is in the meta position in the benzyl radical.

Ethyl benzyl aniline meta-sulfonic acid is investigated as regards absorption in the ultra violet.

Statement of the Problem

The object of this paper is to determine which variables must be more closely controlled in order to obtain more consistent and greater yields in the plant production of ethyl benzyl aniline meta-sulfonic acid.

A further object of this report is to establish the position of the sulfonic acid group as being meta in the benzyl radical by the preparation of derivatives.

Finally, ethyl benzyl aniline meta-sulfonic acid is investigated as to the feasibility of analysis by spectrophotometric method.

Introduction

A search of the literature indicated that there was little
or no published data on the manufacture of ethyl benzyl aniline meta-
sulfonic acid regarding yield. Blangey, Fierz-David and Stamm (1)
indicate a yield of only 71-73% of the meta-sulfonic acid, this being
impure material. It should be noted, however, that the primary
purpose for publishing their paper is to establish the position of the
sulfonic acid group as being meta to the CH_2 group on the benzyl
radical in the above product, and not to establish yields.

It will be shown, that by keeping the volume of caustic
quench used in precipitating the sulfonic acid within certain limits,
an average yield of 91.7% was obtained with a mean deviation of ±0.6%
in a run of six batches, where an attempt was made to limit quenching
volume.

Plant yields at the present time average 87.3% of theory,
fluctuating between a low of about 86% and a high of about 88%.

Cain (2), by a procedure apparently very similar to the one
employed by the writer, indicates that sulfonation of N-ethyl benzyl
aniline takes place in the 4-position on the benzyl radical or para.
Beilstein (3) agrees with the above author. Blangey, Fierz-David
and Stamm (1), however, disagree with both, stating and proving
through derivatives that the sulfonic acid group is in the 3 or meta
position.

In view of the above conflicting information, the structure

of the particular sulfonic acid obtained by the writer was investigated

by the method of Blangey, Fierz-David and Stamm (1).

Derivatives of the sulfonic acid were obtained which prove

that the sulfonic acid group enters in the 3 or meta position under the

particular conditions of the sulfonation.

Nothing could be found in the literature pertaining to whether

ethyl benzyl aniline meta-sulfonic acid absorps in the ultra violet.

It was found that this compound does absorp in the ultra violet.

An effort was made to establish its molar extinction coefficient.

Discussion

Table #1 contains a summary of the data from ten sulfonations of N-ethyl benzyl aniline.

The results of the sulfonations indicate that greater yields are obtainable when the volume of caustic quench for precipitation of the ethyl benzyl aniline meta-sulfonic acid is kept within certain low limits, thereby keeping losses through solubility low. The best yields are obtained at a quench-volume range of from about 1500 to 2100 mls., as indicated by batches 3, 6, 8, 9, and 10. Figure #1 shows a plot of volume of quench or filtrate versus yield in grams of 100% ethyl benzyl aniline meta-sulfonic acid. The yields are found to increase with decreasing quench volume.

Further decrease in volume results in excessive sodium sulfate and sodium bisulfate precipitation. It should be noted here that in plant operation it is not economically feasible or necessary to recrystallize or dry the sulfonic acid. Previous experience has shown that sodium sulfate and sodium bisulfate present in the crude sulfonic acid do not interfere in a following condensation reaction. Sulfates must finally be removed, but at a later more convenient step in the process. At this point it is possible that the added cost of material for sulfate removal could offset the gain resulting from higher yields, which necessitate lower quench volumes and thus greater sulfate precipitation. By observing the range of volumes mentioned above, better yields are realized without excessive sulfate precipitation.

Sulfonations were carried out at 30°, 40°, 50°, and 70°C. in an effort to determine the effect of temperature on yield. A temperature of

Summary of Data on Sulfonations-Batches 1 to 10 Table-#1

| Batch No.	1	2	3	4	5	6	7	8	9	10
Sulfonation Temp.-°C.	30	40	40	50	50	50	50	50	70	70
Sulfonation Time-Min.	44	23	21	17	15	16	14	16	11	12
Quench Time-Min.	15	5	4	10	3	4	3	3	2	2
Vol. of Filtrate-c.c.	3325	2880	1870	3380	2650	1450	1950	1920	2130	2020
*E.B.A. in Filtrate-gr.	--	1.3	negl.	2.4	0.5	negl.	0.5	0.1	1.9	negl.
**E.B.A.S. equiv. to E.B.A.-gr.	--	1.7	--	3.3	1.1	--	0.7	0.1	2.7	--
Yield "as is" E.B.A.S.-gr.	232.1	234.9	320.0	200.6	359.6	396.9	301.7	292.3	272.9	291.7
% Purity of E.B.A.S.	69.0	85.2	66.8	84.1	57.6	53.9	69.8	72.3	77.7	73.7
100% E.B.A.S.-gr.	160.1	200.1	213.8	168.7	207.1	213.9	210.9	211.3	212.0	215.0
% of Theory	68.8	86.3	92.1	72.6	89.3	92.2	90.8	91.2	91.3	92.7

*E.B.A.-N-Ethyl Benzyl Aniline

**E.B.A.S.-Ethyl Benzyl A niline meta-Sulfonic Acid

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Fig.-#1
Volume of Filtrate-c.c.

vs.

Yield of 100% Ethyl Benzyl Aniline meta -Sulfonic-grs.

Batches 1 to 10
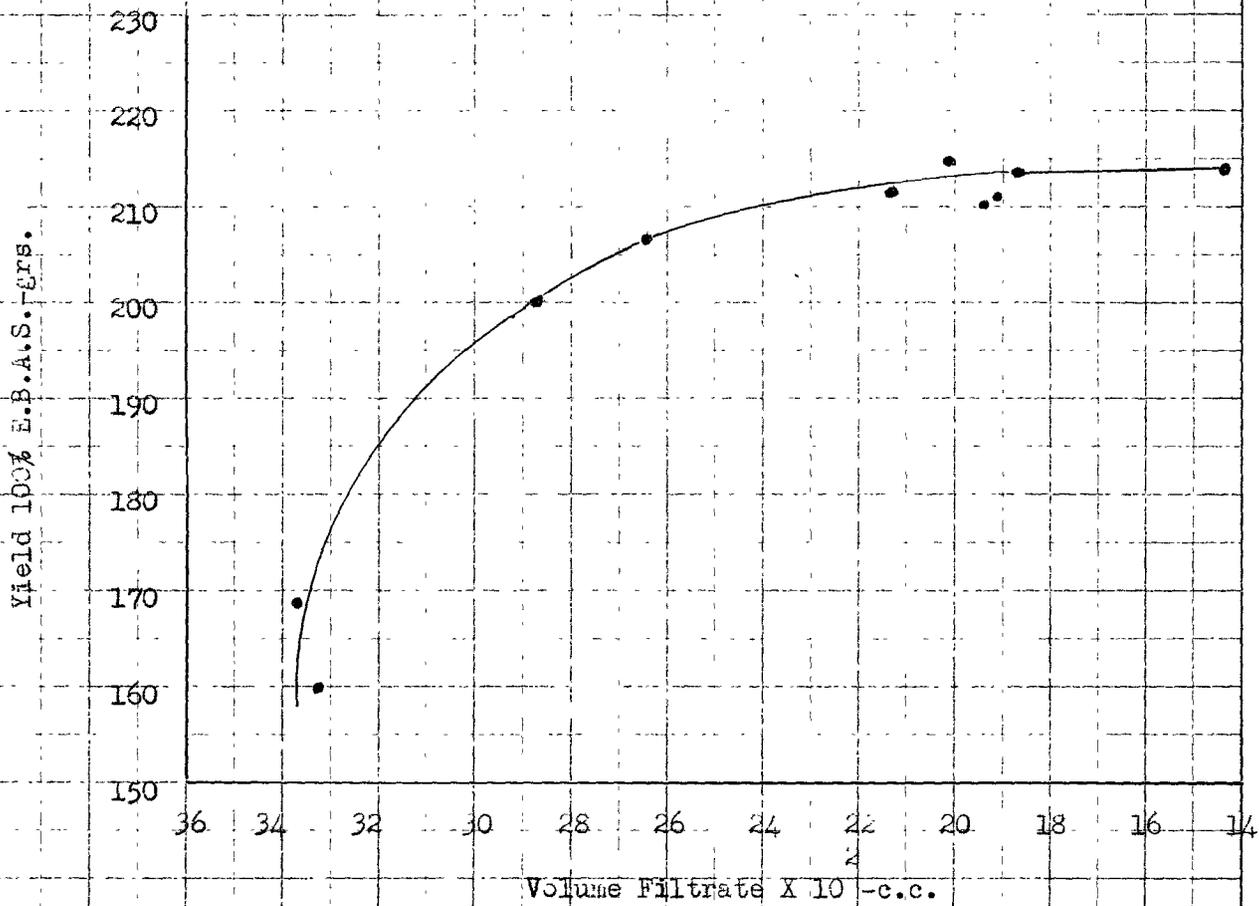
50°C. appears to be too low to carry out the sulfonation. During the sulfonation, it was noted that there was considerable gumming and thus improper mixing of the oleum with ethyl benzyl aniline. This probably accounts in part for the extremely low yield obtained at this temperature (batch #1), the other^factor contributing to the low yield being the high filtrate or quench volume.

Sulfonations carried out at 40°, 50°, and 70° (batches #3, 6, 7, 8, 9, and 10), where an effort was made to keep the volume of the quenches close, show only small variations in yield, the difference between the lowest and highest yield being 1.9%. Batches #2 and #4 were run at 40°C. and 50°C. respectively as above, however, the quench volumes were much higher (2880 ml. and 3390 ml. respectively) and the yields much lower. (86.3% and 72.6%)

Since the sulfonation is so highly exothermic, difficulty may be readily encountered in keeping the reaction at a specific temperature. It is therefore necessary to sacrifice time in sulfonating. The sulfonation is thus carried out at such a rate that, with the cooling system at its maximum capacity, the desired sulfonating temperature is not exceeded.

The ethyl benzyl aniline remaining in the filtrate was extracted in an effort to obtain a material balance. As indicated by the data, no correlation could be made. A possible explanation lies in the fact that varying amounts of the ethyl benzyl aniline are occluded by the sulfonic acid crystals during precipitation.

Figure 11 shows the two methods followed for proving that the sulfonic acid group enters meta to the CH_2 group in the benzyl radical.

Fig. 11

Reactions Involved in Proof of Structure
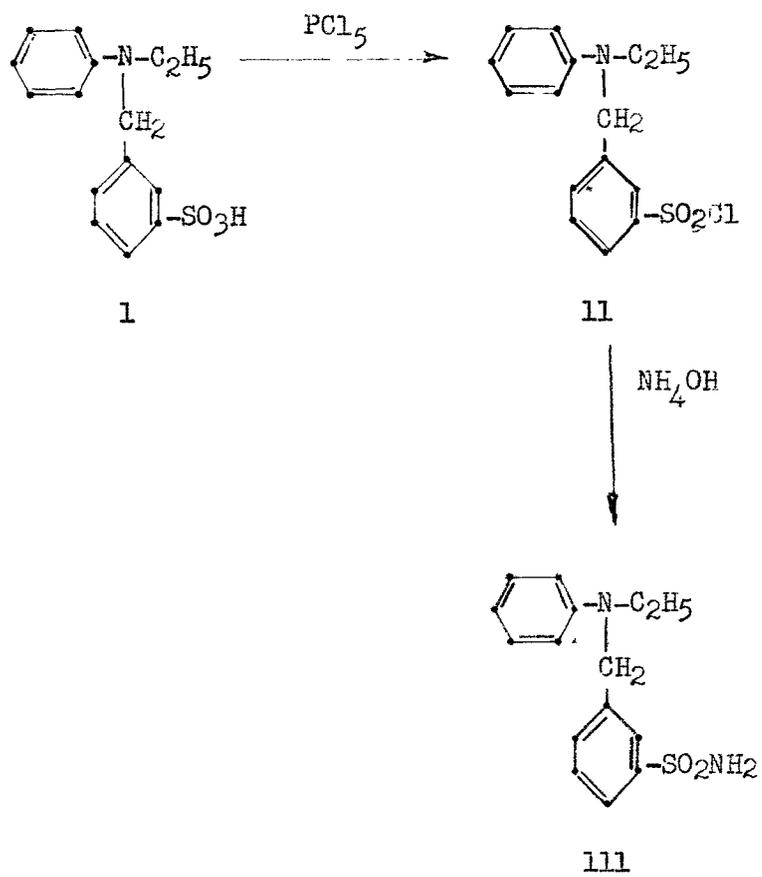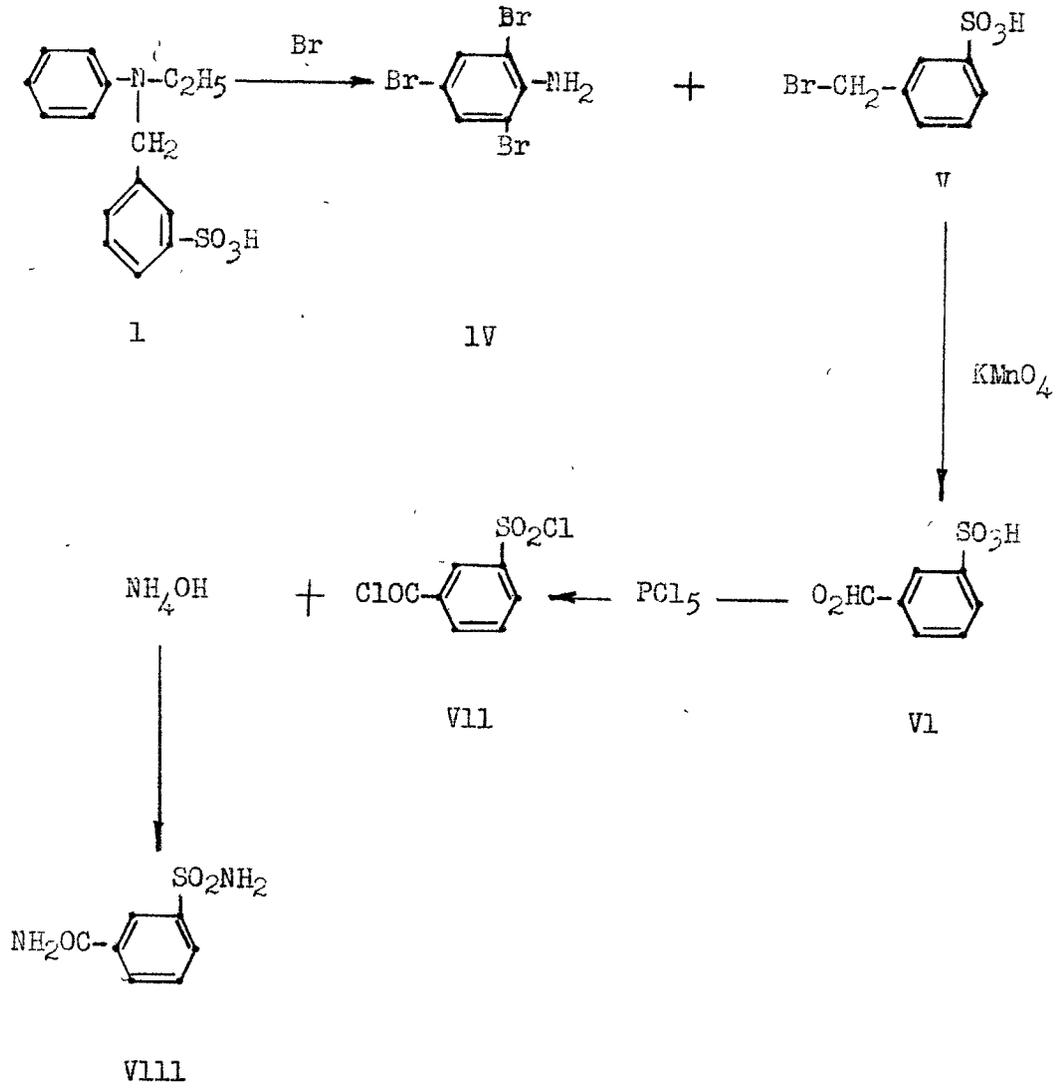
of Ethyl Benzyl Aniline meta-Sulfonic Acid

Fig. 11 (con't.)

In the first reaction the purified sulfonic acid, compound 1, was reacted with PCl$_5$ to form the ethyl benzyl aniline meta-sulfonyl chloride, compound 11. This was in turn reacted with ammonium hydroxide to form an amide. The resulting amide was found to be ethyl benzyl aniline meta-sulfonamide, compound 111, by melting point. It may thus be concluded that the starting material is the meta-sulfonic acid.
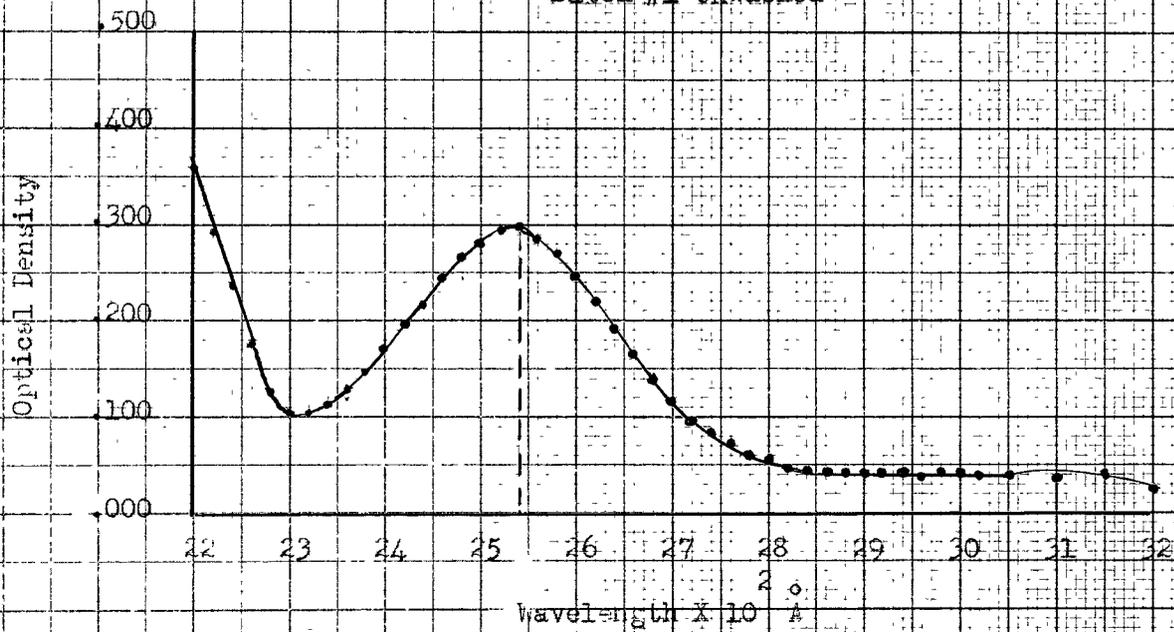
The second reaction involved splitting compound 1, by bromination, into tribromo aniline, compound 1V, and the sodium salt of brom methyl benzene meta-sulfonic acid, compound V. The writer could not isolate the tribromo aniline in an identifiable form. Compound V was oxidized with potassium permanganate and isolated as the sodium salt of meta-sulfobenzoic acid, compound V1. Compound V1 was in turn reacted with PCl$_5$ to form an unstable oil, meta-chorosulfonyl benzoyl chloride, compound V11. Finally compound V11 was converted to a di-mide with ammonia water. The melting point of this compound identified it as benzamide meta-sulfonamide, compound V111. The starting material was thus identified as the meta isomer, ethyl benzyl aniline meta-sulfonic acid, compound 1.

In an effort to determine whether ethyl benzyl aniline meta-sulfonic acid could be analyzed by spectrophotometric means, a twice-recrystallized weighed amount of the sulfonic acid from batch #1 was dissolved in distilled water and scanned in the ultra violet in a range from 2200 Å to 3200 Å. As illustrated by Fig. #3 and Table #2 (Figs. 13, 14 and 15), the sulfonic acid obtained in batch #1 (and subsequent batches randomly selected for analysis) was found to give a characteristic peak in absorption at 2540 Å.
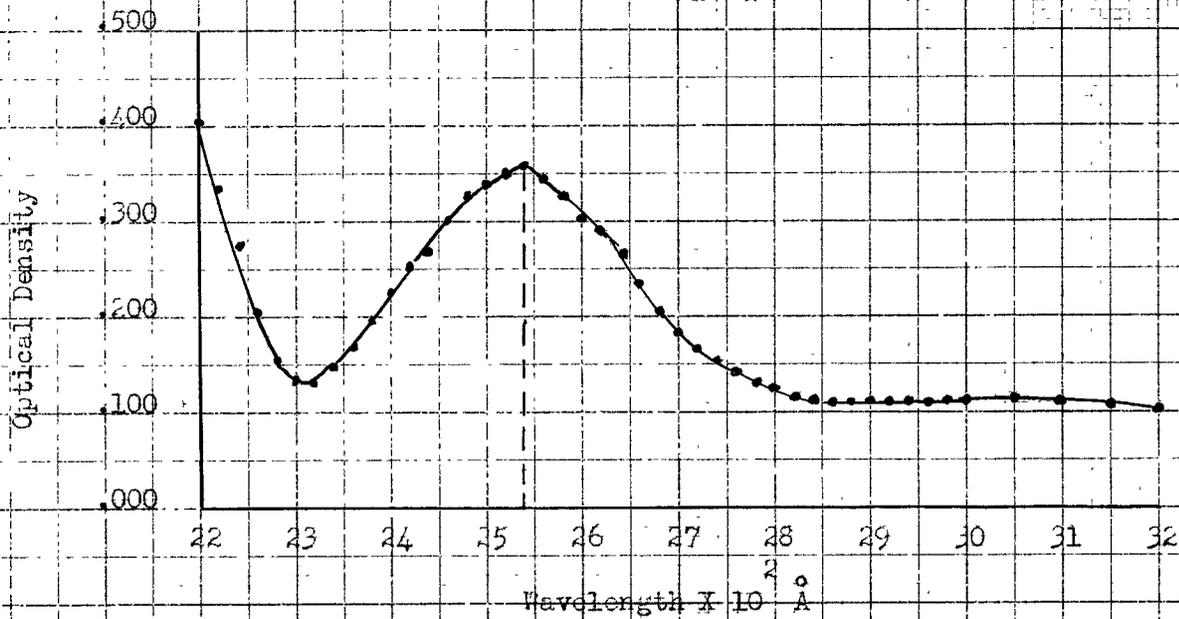
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Fig. #3

Absorption Curves for Ethyl Benzyl Aniline meta-Sulfonic Acid

Batch #1-Unwashed

Batch #1-Washed

Table 11-Absorption Data for Ethyl Benzyl Aniline meta-Sulfonic Acid

Batch #1-Unwashed   Batch #1-Washed

W.L.-Å	O.D.	W.L.-Å	O.D.	W.L.-Å	O.D.	W.L.-Å	O.D.	W.L.-Å	O.D.	W.L.-Å	O.D.
2200	.360	2500	.282	2800	..054	2200	.405	2500	.339	2800	.125
2220	.293	2520	.294	2820	.048	2220	.335	2520	.350	2820	.119
2240	.239	*2540	.296	2840	.046	2240	.275	*2540	.358	2840	.117
2260	.175	2560	.285	2860	.044	2260	.205	2560	.344	2860	.116
2280	.123	2580	.270	2880	.043	2280	.153	2580	.327	2880	.115
2300	.104	2600	.247	2900	.042	2300	.133	2600	.303	2900	.114
2320	.103	2620	.219	2920	.041	2320	.131	2620	.293	2920	.113
2340	.114	2640	.190	2940	.040	2340	.149	2640	.263	2940	.112
2360	.129	2660	.163	2960	.039	2360	.169	2660	.234	2960	.111
2380	.147	2680	.138	2980	.043	2380	.197	2680	.209	2980	.112
2400	.170	2700	.113	3000	.043	2400	.227	2700	.184	3000	.111
2420	.195	2720	.097	3050	.042	2420	.252	2720	.168	3050	.114
2440	.216	2740	.085	3100	.039	2440	.270	2740	.156	3100	.112
2460	.244	2760	.071	3150	.033	2460	.301	2760	.142	3150	.109
2480	.266	2780	.060	3200	.023	2480	.325	2780	.131	3200	.103

*-Maxima in Absorption   *Corr.-.006 Unwashed   *Corr.-.023 Washed

Table 11-Abso ption D ta For Ethyl Benzyl Aniline meta-Sulfonic Acid-con't.

Batch #2-Unwashed		Batch #2-Ether Washed	
W.L.-Å	O.D.	W.L.-Å	O.D.
2500	.361	2500	.295
2520	.376	2520	.305
*2540	.379	*2540	.310
2560	.365	2560	.304
2580	.346	2580	.294
2600	.315	2600	.277
*max.-corr. -.01		*max.-corr. -.008	

Batch #6 Unwashed		Batch #6-Ether Washed	
W.L.-Å	O.D.	W.L.-Å	O.D.
2500	.429	2500	.276
2520	.455	2520	.297
*2540	.460	*2540	.307
2560	.449	2560	.298
2580	.440	2580	.283
2600	.380	2600	.253
*max.-corr. -.012		*max.-corr. -.008	

Table 11-Absorption Data for Ethyl Benzyl Aniline meta-Sulfonic Acid con't

Batch #8-Ether Washed		Batch #9-Ether Washed	
W.L.-Å	O.D.	W.L.-Å	O.D.
2500	.357	2500	.272
2520	.277	2520	.280
*2540	.390	*2540	.287
2560	.376	2560	.285
2580	.362	2580	.272
2600	.333	2600	.248

*max.-.corr. -.006   *max.-.corr. -.006

Table #2 Tabulation of U.V. Results-con't

Batch #	1	2	6	8	9
% purity by titration	99.96	100.05	99.96	99.99	99.99
UNWASHED					
Conc.-mg./100 ml.	1.1	1.3	1.7	----	----
Corrected O.D. at 2540 $\overset{o}{A}$	.302	.393	.472	----	----
E% value	274	302	277	----	----
Molar Ext. Coeff.	7990	8800	8075	----	----
ETHER WASHED					
Conc.-mg./100 ml.	2.3	1.9	1.9	2.4	1.8
Corrected O.D. at 2540 $\overset{o}{A}$	.381	.318	.315	.396	.293
E% value	165	167	166	165	163
Molar Ext. Coeff.	4820	4860	4830	4800	4730

Sample Calculation

Molar Extinction Coefficient—Batch #1 Washed

$$E = \frac{1}{\frac{cl}{M}} \log \frac{I_{\bullet}}{I}$$

E=Molar Extinction Coefficient

c= conc. of sample in gr./l.

l= cell length=1cm.

M= molecular wt. of sulfonic acid= 308

$\log \frac{I_{\bullet}}{I}$ = optical density

Then $E = \frac{1}{\frac{.023 \times 1}{308}} \times .291 = 4820$

Table #2 Tabulation of U.V. Results-concluded

The E % value was determined as follows:

$$E \% = \frac{\text{optical density}}{\text{conc. of sample } (mg./100 \text{ ml.})} \cdot \text{---} \lambda \, 1000$$

where   E = Extinction Cofficient

Then for Batch # 1 Washed,

$$E \% = \frac{.381 \text{ X } 1000}{2.3} = 165$$

Having found that the sulfonic acid had a characteristic maximum absorption in the ultra violet, an effort was made to establish a molar extinction coefficient specification.

In undertaking the last mentioned project, considerable difficulty was encountered. In all samples run, absorption peaks were found to exist at 2540 Å, however, consistent molar extinction coefficient values could not be obtained for different concentrations of the sulfonic acids analyzed, although the compound was supposedly pure as determined by titration. (table #2 pg. 16)

On the assumption that the discrepencies in extinction coefficients could be due to the presence of some impurity that still remained in the sulfonic acid even after purification, and whose presence could not be assuredly detected by ordinary titration method, samples used in the u.v. analyses were washed with ether and reanilyzed. More consistent results were obtainable as shown by table #2, pg. 16.

In scanning a sample of N-ethyl benzyl aniline in an alcoholic solution in a purely qualitative manner for information, it was found to absorp at exactly the same wave length as the sulfonic acid, i.e. at 2540 Å.

Since optical densities at the same wave length are algebraically additive, it is reasonable to assume that the unwashed recrystallized sulfonic acid samples still contained varying small amounts of N-ethyl benzyl aniline. These trace amounts, however, were still detected by the spectrophotometer, giving positive errors in absorption.

To the best knowledge of the writer, the molar extinction coefficient for ethyl benzyl aniline meta-sulfonic acid lies in the range of 4730 to 4860, and correspondingly, the E% between 163 and 167.

Experimental

A. Sulfonation

The sulfonation of N-ethyl benzyl aniline is shown as follows:
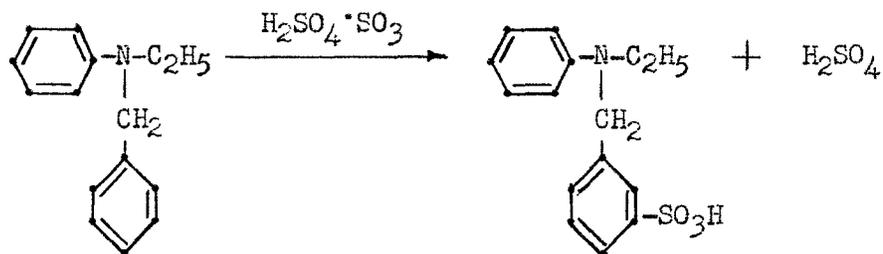
Compound 1

525 grs. of 20% oleum were cooled to 15°C. 168.5 grs. of N-ethyl benzyl aniline were added dropwise to the agitated oleum at such a rate that the different sulfonation temperatures indicated by Table #1 (i.e. 30-40-50 and 70°C.) were obtained. Following the sulfonation, the reaction mixture was stirred one hour at the temperature of sulfonation and then quenched into a sodium hydroxide (280 grs.) water-ice mixture at such a rate that the temperature of sulfonation was not exceeded. The time required for quenching and volume of quench or filtrate appear in Table #1.

The precipitated meta-sulfonic acid was cooled to 25°C., stirred one hour at this temperature, filtered, tamped, and sucked dry.

The semi-dry cake was weighed ("as is weight") and a sample analyzed by titration. (Table #1) It is because of the varying amounts of moisture present in the sulfonic acid after sucking dry on the filter that the "as is weight" shown on Table#1 varies so from batch to batch.

To determine the amount of unreacted N-ethyl benzyl aniline, a 100 ml. sample of the filtrate was extracted with 4 X 25 ml. of ether. The ether was placed in a tared evaporating dish, evaporated to dryness on a steam bath and weighed. The total amounts of N-ethyl benzyl aniline

found in the filtrate are recorded in Table #1.

B. Determination of Structure

Ethyl Benzyl Aniline meta-Sulfonamide lll

31.5 grs. of pure ethyl benzyl aniline meta-sulfonic acid, Compound l, and 34.5 grs. of PCl_5 were added to 125 mls. of dry benzene. After the initial heat of reaction had subsided, the mixture was refluxed on a water bath at 80°C. until the evolution of HCl had stopped and a clear light yellow solution remained.

After cooling, the above solution was poured into 750 mls. of cold water. The oil which separated (impure Compound ll) was redissolved with agitation. The acqueous layer was now extracted with benzene, and the benzene layer was washed with cold water until acid free, as indicated by congo red paper. Sodium sulfate was used to dry the benzene layer.

Upon distilling off the benzene, a pale-brown, viscous, oily residue remained, pure Compound ll. 62.5 mls. of 20% ammonia water were poured over the oil with vigorous shaking. A brown-white product precipitated after overnight standing, impure Compound lll. The cake was broken up, filtered, water washed, and dried. Impure Compound lll melted at 88-89°C.

After recrystallization from hot alcohol, 16.2 grs. (55% of theory) of Compound lll were obtained which melted at 98.2-98.8°C. (lit. m.p. 98-99°C.)

Sodium Salt of meta-Sulfobenzoic Acid Vl

7.3 grs. or 1/40 mole of pure Compound l was dissolved with 1.4 grs. of soda lime and 100 mls. of water. A bromination mixture, consisting of 15 grs. of KBr and 4.2 grs. of $KBrO_3$, was dissolved in 250 mls. of

water and slowly added to the above alkaline solution with agitation.

Following the bromination, the solution was warmed on a steam bath. During the warming, concentrated HCl was added dropwise until bromine vapors began to evolve. Heating was continued for one hour.

During the heating period, a brown oil settled out of solution. After cooling, the oil solidified into a brownish-black amorphous residue. This residue was filtered and dried. The writer did not find it possible to identify this material, since it could not be obtained in a crystalline form. It was assumed to be very impure Compound 1V.

The filtrate from Compound 1V, containing Compound V, was extracted with ether to free it from any residual Compound 1V, and then concentrated to 200mls. on a steam bath. After cooling, 6.5 grs. of pulverized $KMNO_4$ were gradually added to the concentrated solution. Upon heating on a steam bath, bromine vapors began to evolve. Following one hour of heating, the manganese dioxide residue was filtered off and washed with 2 X 20 mls. of hot water, the wash being added to the filtrate.

The filtrate was made slightly acidic with HCl, evaporated to 150 mls. on a steam bath, and saturated with NaCl.

After standing overnight, the mono-sodium salt of meta-sulfobenzoic acid crystallized out in the form of white scales, Compound V1. It was filtered, washed with 10% NaCl and dried. (Yield 2.5 grs.-47.2% theory)

Chlorosulfonyl Benzoyl Chloride V11

2.5 grs. of Compound V1 were mixed thoroughly with 8 grs. of PCl_5 and refluxed with 50 mls. of benzene for one hour using a steam bath. The benzene was distilled off under vacuum, leaving behind a brown oil, Compound V11.

Benzamide meta-Sulfonamide Vlll

Concentrated NH_3 water was slowly added to Compound Vll. After vigorous shaking, a gray-white precipitate appeared. This was filtered and dried. Recrystallization from hot alcohol yielded 0.9 grs. (40% theory) of a grainy white precipitate, Compound Vlll. The melting point of this compound, 176-176.5, compared well with the literature m.p. of benzamide meta-sulfonamide, 176°C.

C. Ultra Violet Analyses

Samples of crude ethyl benzyl aniline meta-sulfonic acid selected at random from Batches 1, 2, 6, 8, and 9 were recrystallized twice from hot water using Nuchar C as a decolorant. Each sample was dried overnight at 100°C.

The purity of the recrystallized sulfonic acid was determined by titration with sodium hydroxide. An approximately one gram sample was accurately weighed and dissolved in 200 mls. of distilled water. The solution was titrated with decinormal sodium hydroxide using phenolphthalein as an indicator. Results appear on Table 11, pg. 16.

For ultra violet analysis an approximately 40 mg. sample of recrystallized Batch #1 was accurately weighed and dissolved in exactly 100 mls. of distilled water. A 5 ml. portion of this solution was pipetted into another 100 ml. volumetric flask and diluted to the mark with distilled water.

Using a Beckman Model DU Spectrophtometer, (with distilled water as a blank) the sulfonic acid was scanned from 2200 Å to 3200 Å to determine whether it exibited a maximum in absorption. A maximum

appeared at 2540 Å. In all subsequent runs on Batches 2, 6, 8, and 9, the characteristic peak appeared at this same wave length. (Table 11, pgs. 14 and 15)

Although the absorption maximum had been established, inconsistencies were found to exist when the molar extinction coefficients were calculated. (Table 11, pg. 16, Unwashed)

In view of the above variations, an effort was made to further purify the samples under investigation.

Samples of each of the batches analyzed by ultra violet were placed in a buchner funnel and washed thoroughly with ether.

In reanilyzing these washed samples by the same forementioned ultra violet method, more consistent results as regards molar extinction coefficient values were obtained. (Table 11, pg. 16, Washed)

Conclusions

It has been shown that the volume of caustic quench, used to precipitate the ethyl benzyl aniline meta-sulfonic acid, bares a direct relation to the obtainable yield. By keeping the quench volume within certain low limits, greater and more consistent yields than formerly obtainable at the Levey Co. are realized.

With the particular conditions under which the sulfonations were run, it has been proven by the use of derivatives that the sulfonic acid group on the ethyl benzyl aniline sulfonic acid compound enters meta to the CH_2 group in the benzyl radical.

Ethyl benzyl aniline meta-sulfonic acid has been found to exibit a maximum in absorption in the ultra violet at a wave length of 2540 Å. The molar extinction coefficient value for this compound was shown to be in a range of from 4730 to 4860.

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