[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

SOME DERIVATIVES OF ETHYLBENZENE[1]

BY E. L. CLINE[2] AND E. EMMET REID

RECEIVED AUGUST 29, 1927 PUBLISHED DECEMBER 10, 1927

Because of the close structural relationship to benzene and toluene, ethylbenzene has been a subject for investigation by several workers. These, however, had small quantities of material and many discrepancies are evident in the records of their results.

Recent researches[3,4] have led to the development of a method for the production of ethylbenzene in large quantities. We, therefore, undertook the preparation of some new derivatives of ethylbenzene in order to make further comparisons and at the same time to straighten out the literature on some of the previously prepared compounds.

Historical

Beilstein and Kuhlberg,[5] two of the earliest workers in this field, found an almost complete analogy between the nitro and amino compounds of toluene and ethylbenzene. Vorländer[6] found that ethylbenzene acts more like benzene than toluene when treated with hydrocyanic acid, cyanogen, acid chlorides and acid cyanides. The same author further states that ethylbenzene does not react to give an aldehyde by the Gattermann-Koch synthesis, in which statement he is corroborated by several other investigators. However, J. von Braun and Hans Engel[7] report the preparation of *p*-ethylbenzaldehyde by means of this reaction, so that, in this case, ethylbenzene reacts more like toluene than benzene.

Schultz and Flachsländer[8] prepared a series of dyes of the Congo type from benzidine, toluidine and the corresponding ethylbenzene base. They found that the Congo type prepared from diethylbenzidine had a greater solubility, greater coloring power but less resistance to light than that from the other two benzidines. However, they stated that the actual differences were very small.

Beilstein and Kuhlberg,[5] Schultz and Flachsländer[8] and Béhal and Choay[9] have studied the nitration of ethylbenzene and the separation of *o*- and *p*-nitro-ethylbenzenes. Beilstein and Kuhlberg attempted to separate the two isomers by differences in their melting points. After twenty

---

[1] Read at the Baltimore meeting of the American Chemical Society, April, 1925.

[2] From the Ph.D. dissertation of E. L. Cline, Johns Hopkins University, 1925.

[3] Milligan and Reid, THIS JOURNAL, **44**, 206 (1922).

[4] Berry and Reid, *ibid.*, **49**, 3142 (1927).

[5] Beilstein and Kuhlberg, *Ann.*, **156**, 206 (1870).

[6] Vorländer, *Ber.*, **44**, 2461 (1911).

[7] Von Braun and Engel, *Ann.*, **436**, 299 (1924).

[8] Schultz and Flachsländer, *J. prakt. Chem.*, [2] **66**, 160 (1902).

[9] Béhal and Choay, *Bull. soc. chim.*, [3] **11**, 208 (1894).

fractionations, they were not successful in getting complete separation, since the melting points are only nine degrees apart in contrast to the corresponding nitrotoluenes, where there is a difference of 61.5°. Schultz and Flachsländer fractionated eighty times in a vacuum in two-degree cuts to get two fractions 220–230° and 245–250° with a small intermediate fraction. Then they fractionated one hundred times at atmospheric pressure to obtain constant-boiling fractions at 223–224° for the *ortho* and 241–242° for the *para* isomer. Even with this painstaking procedure, the boiling points of the two isomers are wrong, due, perhaps, to defective thermometers.

The Present Investigation

The ethylbenzene was prepared according to a modification of the method of Milligan and Reid.[3] Purified ethylene was introduced into benzene containing aluminum chloride, the mixture being stirred at the rate of 11,000 r.p.m. by a Witt stirrer, as described by Milligan and Reid.[10]

These investigators found that an "incubation period" of an hour or more was necessary to secure maximum absorption of the ethylene, whereas, if they used some of the higher ethylated benzenes (tri- to hexaethylbenzene), along with the above ingredients, the rate of absorption of the ethylene was greatly increased. With these facts in view, a process was worked out by which about 50% of the benzene used could be directly converted into ethylbenzene or, by returning the higher ethylated benzenes to the reaction flask, practically all of the benzene can be converted into ethylbenzene, due to the transfer of the ethyl groups from the higher alkylated ethylbenzenes to the free benzene.[11]

Ethylbenzene was nitrated below 40°, thus avoiding to a large extent the formation of higher nitrated products. Instead of using the tedious method of fractional crystallization, as carried out by Schultz and Flachsländer, we built a high-precision vacuum still, similar to that described by Peters and Baker.[12]

Instead of the main outer glass jacket, we used a brass tube 5 cm. in diameter which was connected to two lead tubes leading to and from a xylene reservoir. The temperature of this jacket was maintained at about 140° by the boiling xylene instead of being electrically heated as described by the authors mentioned above. Except for some other minor details, the still was as described by Peters and Baker. By means of this still we were able to separate the *o*- and *p*-nitro-ethylbenzenes sharply by one distillation. This avoided high temperatures as well as loss of time and materials by repeated fractionation.

Beilstein and Kuhlberg obtained equal parts of the two nitro isomers,

---

[10] Milligan and Reid, *Ind. Eng. Chem.*, **15**, 1048 (1923).

[11] Anschütz and Immendorff, *Ber.*, **18**, 657 (1885).

[12] Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

Schultz and Flachsländer report two parts of the *ortho* to one of the *para*, while Behal and Choay found one and a half parts of the *ortho* to one of the *para*. Our results averaged one and two-tenths parts of the *ortho* to one of the *para*. The boiling point of *o*-nitro-ethylbenzene is 135° at 37 mm. and that of *p*-nitro-ethylbenzene 154° at the same pressure.

Both the *o*- and *p*-nitro-ethylbenzenes are quite difficult to reduce to the corresponding amines. All of the earlier workers used tin and hydrochloric acid for both of these reductions but none of them report anything concerning the ease of reduction or the yields obtained. According to our observations this method is excellent in working with the *para* compound, the yield being about 90%, but with the *ortho* compound the yields are poor, probably on account of the entrance of chlorine into the ring as is the case in the reduction of *o*-nitrotoluene.[13,14] The *para* isomer gives yields up to 80% with iron filings and hydrochloric acid but it is almost impossible to effect a complete reduction of the *ortho* isomer with these reagents. Ammonium sulfide in boiling alcohol solution is a good reducing agent for the *para* compound but is very slow with the *ortho*.

The reduction of 2,4-dinitro-ethylbenzene with ammonium sulfide has been studied by Schultz,[15] who claimed to have obtained the 2-nitro-4-amino-ethylbenzene which had a melting point of 43°, with an acetyl derivative melting at 101°. We obtained proof that this reduction yields a mixture of 2-nitro-4-amino-ethylbenzene and the isomeric 2-amino-4-nitro-ethylbenzene. The former is an orange-yellow, crystalline solid which, after recrystallizing from alcohol, melts at 45° and gives an acetyl derivative melting at 110°. We were unable to isolate the latter in the pure form but we were successful in proving its presence by diazotizing a portion of the isomeric nitro-amino compounds and replacing the diazonium group with hydrogen. The products, *o*- and *p*-nitro-ethylbenzenes, were treated with zinc and hydrochloric acid, which would reduce the *para* and not affect the *ortho* isomer. The *p*-amino-ethylbenzene was separated from the *o*-nitro-ethylbenzene and an acetyl derivative prepared which, when recrystallized from water, melted at 94.5°, which is the melting point given for 4-acetylamino-ethylbenzene.

With these facts in view, there is little doubt that the low melting point given by Schultz for 2-nitro-4-acetylamino-ethylbenzene was due to the presence of an isomer.

The reduction of 2-4-dinitrotoluene with ammonium sulfide gives two isomers also, but due to the difference in stability of their hydrochlorides both have been isolated. We tried to separate the isomeric aminonitro-

---

[13] Bamberger, *Ber.*, **28**, 251 (1895).

[14] Hurst and Thorpe, *J. Chem. Soc.*, **107**, 934 (1915); *C. A.*, **9**, 2887 (1915).

[15] Schultz, *Ber.*, **42**, 2634 (1909).

ethylbenzenes by the same method but, due to the small percentage of 2-amino-4-nitro-ethylbenzene, which gives the less stable hydrochloride, we were unable to obtain it in the pure form.

From the *o*- and *p*-amino-ethylbenzenes, a number of derivatives have been prepared and their properties studied; among these is a series of azo dyes prepared from aniline, *o*- and *p*-methylaniline and *o*- and *p*-ethylaniline. The purpose in making these dyes was to determine the effect of the ethyl groups in comparison with the methyl group.

A distinct deepening in color is noticed in going from aniline to the methylaniline dye and a slight deepening in going from methylaniline to ethylaniline. In both the methylaniline and the ethylaniline series, the *para* isomer gives deeper shades than the *ortho*.

Experimental

Ethylbenzene.—Into a mixture of 300 g. (3.84 moles of benzene), 100 g. of higher ethylated benzenes, 15 g. of aluminum chloride (0.056 moles) and the lower layer from a previous experiment, three equivalents of ethylene were introduced in the course of two hours, the temperature being held between 70 and 80°. The ethylene was passed under the head of the Witt stirrer which was running at 11,000 r.p.m. After the addition of the ethylene, the reaction mixture was allowed to settle. It separated into two distinct layers, the top containing practically all of the hydrocarbons with a very little aluminum chloride and the lower which contained nearly all of the catalyst. This was left in the flask for the next run. The top layer was siphoned off, poured onto ice, washed and dried over calcium chloride and fractionated through a 90cm. punched-in column. By the first distillation it was divided into four fractions: one boiling between 80 and 100°, which was returned to the reaction vessel as benzene; one boiling from 100–150°, the ethylbenzene fraction; one boiling between 150 and 190°, the diethylbenzene fraction and a residue which was returned to the reaction vessel as higher alkylated benzenes. The ethylbenzene and the diethylbenzenes were purified in one distillation by passing them through the high-precision still. After purification, ethylbenzene boiled at 135°. Treating 300 g. of benzene with three equivalents of ethylene, the averages for seven runs were: recovered benzene 29 g., ethylbenzene 215 g., diethylbenzene 105 g., residue 39 g.

_o_- and _p_-Nitro-ethylbenzene.—Into 700 g. (6.6 moles) of ethylbenzene, contained in a two-liter flask cooled by ice, a mixture of 510 g. of concd. nitric acid (sp. gr. 1.42) and 675 g. of concd. sulfuric acid was allowed to flow, dropwise, in the course of six hours. The contents of the flask was agitated with a Witt stirrer, revolving at 3000 r.p.m. and the temperature kept below 40°. After the addition of the acid, the mixture was stirred for three hours at room temperature and then the temperature was gradually raised to 100° in the course of four hours and kept there for two hours. The product was allowed to settle and the oil separated from the excess acid. The oil was washed several times with water, then with caustic soda solution and finally with water. It was distilled with steam in order to separate the mononitro-ethylbenzenes from the higher nitrated products. The oil remaining in the flask was principally 2-4-dinitro-ethylbenzene, previously described by Weisweiller.[16]

The oil volatile with steam was dried over calcium chloride and fractionated, using the high-precision vacuum still. The entire inner column was kept at 140° by the xylene vapors in the jacket. In the distilling flask was placed 760 g. of the nitro-ethylbenzenes

---

[16] Weisweiller, *Monatsh.*, 21, 39 (1900).

and the pressure of the whole system brought to 37 mm. At this pressure the *o*-nitro-ethylbenzene distils at 135° while the *para* isomer boils at 154°. The water in the dephlegmator was regulated so that nine-tenths of the vapors was condensed. After practically all of the *ortho* compound has passed over the distillation ceases. At this point a cut is made. The liquid in the receiver is pure *o*-nitro-ethylbenzene, amounting to 384 g. The distillation is again resumed at 30 mm. and continued until the rate of distillation again slows down, when the pressure is lowered a few more millimeters. This process is continued until the temperature remains constant during the distillation of 30 cc., when it is stopped. The intermediate fraction (60 g.) is a mixture while that in the distillation flask is pure *p*-nitro-ethylbenzene (317 g.). Thus we were able to secure in the pure form 50.5% of *o*- and 41.7% of *p*-nitro-ethylbenzene.

Reduction of *p*-Nitro-ethylbenzene.—A mixture of 120 g. of granulated zinc and 75 g. of *p*-nitro-ethylbenzene was placed in a two-liter flask equipped with an air condenser. To this was added 250 g. of concd. hydrochloric acid in small portions, heat being applied at intervals. After all of the acid had been added, the mixture was heated on a water-bath for two hours to complete the reaction. The mixture was then made strongly alkaline with caustic soda and steam distilled. The distillate was saturated with salt, extracted with ether and the resulting solution dried and distilled; yield, 90%.

By reduction with iron filings and 10% hydrochloric acid, a yield of 80% was obtained.

Reduction of *o*-Ethyl-benzene.—Tin and hydrochloric acid gave a yield of 70% of *o*-nitro-ethylbenzene. With iron filings and 10% hydrochloric acid the reduction was not complete in sixteen hours at 130° so this method was abandoned.

Reduction of 2-4-Dinitro-ethylbenzene.—A solution of 50 g. of 2-4-dinitro-ethylbenzene in 150 g. of ethyl alcohol was treated with 150 g. of concd. ammonia water. The mixture was then alternately saturated with hydrogen sulfide and boiled until a gain in weight of 30 g. was effected. The solution was poured onto ice and the amine separated out. It was filtered off and dissolved in dilute hydrochloric acid. The acid solution was boiled with animal charcoal, filtered and allowed to cool. The hydrochloride separating out was purified by recrystallization several times from dilute acid, using animal charcoal each time. The free base was set free by ammonia and recrystallized from dilute alcohol. It melted at 45°. The sulfate was prepared by treating the amine with dilute sulfuric acid. It is slightly soluble in water but soluble in ordinary solvents. The acetyl derivative was prepared by treating the amine with acetyl chloride. It is soluble in alcohol and slightly soluble in water. When recrystallized from alcohol it melted at 110°.

Analyses. Amine hydrochloride for HCl: Calcd. 18.94. Found: 18.67, 18.61.
Amine sulfate for S: Calcd. 7.45. Found: 7.55, 7.37.
Acetyl derivative for N: Calcd. 13.46. Found: 13.18.

Amine Salts of **Anthraquinone-1-butyl-thio-ether-5-sulfonic Acid.**—The salts of *o*- and *p*-ethylaniline were prepared according to the method of Reid, Mackall and Miller.[17] It was thought that possibly the ethyl group would lower the melting point enough to avoid decomposition and that these might prove good compounds for identification. However, they showed melting points with decomposition similar to the compounds of the toluidine. The following is a comparison with similar compounds prepared from *o*- and *p*-methylaniline.

Methylaniline		Ethylaniline	
ortho	*para*	*ortho*	*para*
234–237°	256–260°	237–239°	247–249°

---

[17] Reid, Mackall and Miller, THIS JOURNAL, **43**, 2104 (1921).

Anal. *Ortho* ethyl compound, calcd. for $C_{26}H_{27}O_4NS_2$: S, 12.92. Found: 12.68, 12.86.

Para ethyl compound, calcd. for $C_{26}H_{27}O_4NS_2$: S, 12.92. Found: 13.13, 13.93.

Sulfonation of *p*-Ethylaniline.—Sulfonations of *p*-methylaniline and of *p*-ethylaniline were carried out under the same conditions. Equally good results were obtained with both compounds. In both cases the sulfonic acid group enters the ring *ortho* to the amino group. A mixture of 30 g. of *p*-amino-ethylbenzene and 75 g. of concd. sulfuric acid was kept at 180° until sulfonation was complete. The reaction mixture was poured into 300 g. of water when the free sulfonic acid separated out in the form of white needles. It was recrystallized from water.

In order to determine the position of the sulfonic acid group in the ring, a portion of the acid was diazotized and the diazonium group replaced by a hydrogen atom. By the usual method the sulfonic group was converted into its sulfonamide which, after recrystallization from alcohol, melted at 86°, corresponding to the *m*-ethylsulfonamide described by Semptowski.[18]

The helianthine dye prepared by diazotizing this amine and coupling with dimethylaniline resembles very closely helianthine and *p*-methylhelianthine.

Anal. Calcd. for $C_8H_{11}O_3NS$: S, 15.92. Found: 16.17, 15.73.

3-5-Dibromo-4-amino-ethylbenzene.—One equivalent of *p*-ethylaniline hydrochloride dissolved in water was treated with four equivalents of bromine. The solid which separated out was crystallized from alcohol as long, silky, white, thread-like crystals melting at 85°. The corresponding reaction with chlorine yields a pasty mass which could not be purified.

Anal. Calcd. for $C_8H_9Br_2N$: Br, 56.76. Found: 56.32.

Diazo-amino-ethylbenzene.—This compound was prepared by diazotizing aniline and coupling it with *p*-ethylaniline and by the reverse process. The same compound was formed in each case. Aniline (10 g.) was dissolved in a solution of 100 g. of water and concd. hydrochloric acid corresponding to 12 g. of the free acid, and diazotized. This was treated with a solution of 13 g. (0.107 mole) of *p*-ethylaniline in the theoretical amount of acid. A saturated solution of 50 g. of sodium acetate was added with stirring and the reaction mixture allowed to stand for several hours. The compound which separated out was filtered off, pressed on a porous plate and recrystallized from petroleum ether. It crystallized in yellow needles which melted at 75°.

Anal. Calcd. for amino nitrogen: 5.96. Found: 6.16.

***o*-Amino-azo-ethylbenzene.**—We were unable to isolate this compound in the pure state since it forms an oil which cannot be distilled without decomposition and does not solidify at 20°.

***o*-Ethylphenylhydrazine.**—*o*-Ethylphenylhydrazine hydrochloride was prepared by the ordinary methods for the preparation of hydrazines. It was pressed on a porous plate and recrystallized from dilute acid. The free *o*-ethylphenylhydrazine was prepared by warming the hydrochloride with caustic soda solution. It was then extracted with ether. In the free state it is a very unstable liquid, boiling at 156° at 28 mm. and melting at 49–50°. Its hydrochloride forms hydrazones readily. When *p*-tolylaldehyde is treated with an aqueous solution of the hydrochloride, a hydrazone is formed. It decomposes rapidly in the air. After recrystallizing from alcohol, it melted at 102.5–103°.

Anal. Calcd. for $C_8H_{12}N_2.HCl$: HCl, 21.01. Found: 20.81.

***o*-Ethylphenylhydroxylamine.**—Attempts to prepare this compound by all standard

---

[18] Semptowski, *Ber.*, 22, 2673 (1889).

methods were unsuccessful. The reduction of *p*-nitro-ethylbenzene with zinc dust in neutral solution does not take place at low temperatures and at a higher temperature the azoxy derivative is formed in small quantities. Zinc dust in alcoholic solution gives a good yield of the azoxy compound. Ammonium sulfide in alcoholic solution has no effect in the cold, while at higher temperatures it gives the amine.

***p*-Ethylazoxybenzene.**—In attempting to prepare the *p*-ethylphenylhydroxylamine by the method used by Bamberger[19] for *p*-methylphenylhydroxylamine, we obtained the *p*-ethylazoxybenzene. This is a striking difference between the behavior of the two nitro compounds.

A water solution of 2.4 g. of calcium chloride was added to a mixture of 28 g. of *p*-nitro-ethylbenzene dissolved in 70 g. of ethyl alcohol. The mixture was boiled under reflux for a half hour during which time 30 g. of zinc dust was added in portions. The zinc oxide was filtered off and the filtrate poured into water. The oil which separated was steam distilled to remove any volatile impurities. When cooled it solidified and was recrystallized from alcohol.

When *p*-ethylazoxybenzene was distilled from iron filings, it gave *p*-ethylazobenzene, which is described by Schultz,[20] m. p. 63°.

***p*-Ethylbenzaldehyde.**—We attempted to prepare the *p*-ethylbenzaldehyde from ethylbenzene and carbon monoxide by means of the Gattermann-Koch reaction, using high-speed stirring to accelerate the reaction. Only a trace of the aldehyde was formed.

Azo Dyes from Aniline, *o*- and *p*-Methylaniline and *o*- and *p*-Ethylaniline.—Aniline, *o*- and *p*-methylaniline and *o*- and *p*-ethylaniline were diazotized and coupled with Schollkopf's acid and *p*-methylaniline and *p*-ethylaniline with Neville and Winther's acid. Two per cent. dyeings were made on wool skeins, using standard methods for application.

An attempt to isolate the dye from *o*-ethylaniline and Neville and Winther's acid was a failure. The coupling was complete but the solubility of the dye was so great that it could not be salted from solution.

There is a marked change in the color of the dye in going from aniline to methylaniline and a slight deepening in the color in going from methylaniline to ethylaniline. In both the methylaniline and ethylaniline series the *para* dye was deeper in shade than the *ortho*.

The two dyes prepared from *p*-ethylaniline were obtained by recrystallization from alcohol.

Summary

1. An improvement has been made upon the procedure for the preparation of ethylbenzene from benzene and ethylene in the presence of aluminum chloride.
2. The isomeric *o*- and *p*-nitro-ethylbenzenes were separated by one distillation through a high-precision vacuum still, thus eliminating the waste of materials and time necessitated by the older method of fractional distillation.
3. The nitro compounds were reduced to the corresponding amines, and from these amines several new derivatives were prepared.
4. A series of azo dyes was prepared from aniline, *o*- and *p*-methylaniline and *o*- and *p*-ethylaniline to determine the relative effects of the methyl and ethyl groups.

BALTIMORE, MARYLAND

---

[19] Bamberger, *Ber.*, 31, 582 (1898)

[20] Schultz, *Ber.*, 17, 475 (1884).