

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE ETHYLATION OF BENZENE AND NAPHTHALENE.

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It has long been known that benzene may be ethylated to form ethylbenzene, di-ethyl-, triethyl-, etc., even up to hexa-ethylbenzene when it is treated with ethyl chloride in the presence of aluminum chloride according to the Friedel and Crafts reaction.

Balsohn¹ substituted a mixture of ethylene and hydrogen chloride for ethyl chloride, assuming that the two would unite to form ethyl chloride which would then react. As hydrogen chloride is regenerated in the reaction, very little of it need be present. In fact Balsohn found that the preparation could be carried out without the addition of any hydrogen chloride; apparently aluminum chloride in the presence of traces of water, etc., furnished sufficient hydrogen chloride to keep the reaction going.

He used 400 g. of benzene with 50 g. of aluminum chloride and passed ethylene into the mixture for "several days" at 70° to 90°, thus obtaining 170 g. of ethylbenzene, 135 g. of di-, 75 g. of tri-ethyl benzene and 20 g. of higher-boiling products. From these figures it appears that about 154 g. of ethylene had been taken up. As he passed in 280 g. of ethylene, only 55% of it was absorbed.

Under the conditions described by Balsohn, this preparation is tedious as to time and wasteful of material, and as a matter of fact does not seem to have come into general use.

The Present Investigation.

It seemed to us likely that efficient stirring might so increase the contact of the ethylene with the aluminum chloride and benzene that this would become a practical method of ethylating benzene and its homologs. Experiment has verified this prediction.

According to McDaniel,² benzene dissolves 3 volumes of ethylene at 22°, 2.5 volumes at 50° and probably not over 2 volumes at 80°. The dissolved ethylene may react ever so rapidly, but the formation of the product will be slow unless the solution is re-saturated quickly.

With high-speed stirring it has been found possible to cause benzene containing aluminum chloride to react with 8 volumes of ethylene per minute, the ethylene being totally absorbed so that ethyl benzene and its higher ethylated homologs become readily available. We have used a rapidly rotating metal stirrer of the Witt³ type. The horizontal cross piece is replaced by a disc 37 mm. in diameter by 4 mm. thick with eight

¹ Balsohn, *Bull. soc. chim.*, [2] 31, 539 (1879).

² McDaniel, *J. Phys. Chem.*, 15, 605 (1911).

³ Witt, *Ber.*, 26, 1696 (1893).

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2mm. radial holes which open into a central cavity. The lower vertic portion was replaced by a bell-shaped extension about 15 mm. in diameter and extending downward about 5 mm. The ethylene was delivered by a tube which terminated just below this bell so that the bubbles were drawn through the stirrer and broken up by its rapid rotation.

The stirrer was run at ten to twelve thousand r. p. m. For large scale operations a stirrer of the type proposed by Thoens⁴ or by Ittner⁵ would doubtless be more efficient.

The reaction is best carried on at 70–90°. With efficient stirring the absorption of the ethylene is extremely rapid after an incubation period till about 4 moles of ethylene are absorbed for 1 of benzene, and decreases thereafter.

The ethylene is purified and dried by passing it through towers or wash-bottles filled with suitable materials. It is passed in at such a rate that it is almost totally absorbed. If too much gas is delivered, hydrogen chloride is carried out and the reaction slows, in which case the original speed may be restored by passing in some hydrogen chloride.

It is not possible to conduct the reaction so as to form a single product since some di-ethyl-benzene is formed even before all of the benzene is attacked, but when 1 mole of ethylene is used to 1 of benzene, as in Expt. 3 below, more than half of the product is mono-ethyl-benzene. In Expt. 4, 7.4 moles of ethylene were absorbed by 2.5 of benzene and 272 g., or 1.67 moles of tri-ethyl-benzene obtained, accounting for 5 out of 7.4 moles of ethylene added.

After the reaction is run for a time, if the mixture is cooled it separates sharply into layers, the upper, practically clear and very liquid, the lower, dark and viscous. It is best to work up the two layers separately. The upper layer contains only a trace of aluminum chloride and consists of unchanged benzene with the lower ethylation products and relatively small amounts of the higher. The liquid is shaken with acidulated water, dried and fractionated. The lower layer, which is much the smaller, contains practically all of the aluminum chloride associated with higher ethylated benzenes, particularly penta-ethyl-benzene. It may be worked up by pouring upon ice and hydrochloric acid; it is then washed, dried and fractionated under reduced pressure in the case of the high-boiling portion.

The hexa-ethyl-benzene fraction solidifies and is centrifuged and washed with a little alcohol. It is readily obtained as a snow-white solid. The highest fractions contain a fluorescent oil which cannot be any ethyl-benzene. It is possible that a small portion of the ethylene condenses with itself in the presence of the aluminum chloride before reacting with the benzene.

⁴ Thoens, U. S. pat. 641,561, 1900.

⁵ Ittner, U. S. pat. 1,242,445; *C. A.*, 12, 110 (1918).

The lower viscous layer, if kept away from moisture, may be used for another run with the addition of a small amount of fresh aluminum chloride. In this way we have used the same aluminum chloride in 6 successive runs. This viscous layer appears to be analogous to the so-called "ferment" used in the manufacture of toluene from solvent naphtha.

Results.

In Table I are given the results of 5 runs and in Table II the fractionation of the upper layer.

TABLE I

Expt.	Benzene		Aluminum chloride G.	Cc. per min.	Ethylene absorbed		Ratio
	Wt. G.	Moles			Wt. G.	Moles	
1	200	2.5	50	400-600	62	2.2	1:0.88
2	200	2.5	50	1500-2000	59	2.1	1:0.84
3	200	2.5	50	1500-2200	70	2.5	1:1
4	200	2.5	50	2500	205	7.4	1:2.96
5	700	9.0	100	2000-2500	250	8.9	1:0.99

TABLE II

Fractionation of the Products

Expt.	Benzene 80-100° G.	Ethyl- 100-150° G.	Di-ethyl- 150-190° G.	Tri-ethyl- 190-230° G.	Residue G.
1	52	124	54	7	5
2	56	112	56	8	14
3	42	145	67	...	15
4	0	5	72	272	38
5	236	478	167	40	21

It has been shown by Radziewanowski⁶ and by Boedtker and Halse⁷ that ethyl groups, as other alkyls, may be removed or shifted from one molecule to another in presence of aluminum chloride. In one experiment 250 g. of benzene and 175 g. of the fraction 230-280°, which contained the tetra-, penta-, and hexa-ethyl-benzenes were stirred and heated for 3 hours with the "ferment" remaining from a previous run in which 25 g. of aluminum chloride had been used. At first sight one would not think that stirring would aid in this reaction, but the "ferment" is very heavy and settles quickly unless the stirring is kept up. In a comparative run which was not stirred, there was little transformation.

On fractionation of the upper layer, 102 g. of benzene, 194 g. of mono-ethyl-, 77 g. of di-ethyl-benzene and 18 g. of higher compounds were obtained. It is thus possible to convert a given amount of benzene and the proper amount of ethylene almost completely into ethyl-benzene, or into the di- or tri-ethyl-benzene as desired.

The Ethylation of Naphthalene.

By the action of ethyl chloride on naphthalene Marchetti⁸ obtained

⁶ Radziewanowski, *Ber.*, **27**, 3235 (1894).

⁷ Boedtker and Halse, *Bull. soc. chim.*, [4] **19**, 446 (1916).

⁸ Marchetti, *Gazz. chim. ital.*, **11**, 265, 439 (1881).

ethyl-naphthalene, but in poor yield. Roux⁹ obtained much better results if ethyl bromide and particularly if the iodide was employed, and showed that the β isomer is the one obtained. He tried in various ways¹⁰ to substitute ethylene for the halide but could isolate no ethyl-naphthalene from the products. Fischer and Schneider¹¹ found no reaction between ethylene and naphthalene at 100–200°. We endeavored to effect this reaction by the aid of high speed stirring but without success.

Knowing that phthalic anhydride reacts with the naphthalene in a mixture of benzene and naphthalene in presence of aluminum chloride, we passed ethylene into a solution of 260 g. of naphthalene in 260 g. of benzene with 50 g. of aluminum chloride with the usual high-speed stirring at 80° but the maximum absorption was only 100 cc. per minute so this was abandoned.

Niggemann¹² boiled naphthalene with solvent naphtha and aluminum chloride but obtained no definite indications of the methylation of the naphthalene at the expense of the solvent. However, the ethylation of naphthalene can be readily accomplished by the transfer of ethyl groups from benzene in the presence of aluminum chloride aided by high-speed stirring, as shown by the following experiment.

A mixture of 500 g. of naphthalene, 400 g. of di-ethyl-benzene, 160 g. of ethyl-benzene, total 1060 g., and the ferment from 60 g. of aluminum chloride was stirred at 10,000 r. p. m. for 5 hours at 80°. The clear top layer was separated, washed, dried and fractionated through a good column. This gave 22 g. of benzene, 295 g. of ethyl benzene, 163 g. of diethyl benzene, 256 g. of naphthalene, 170 g. of ethyl-naphthalene, and 140 g. of higher products; total, 1046 g. That the stirring is very advantageous was shown by a parallel experiment in which a similar mixture was heated for 24 hours in a boiling water-bath without stirring. From the product 410 g. of naphthalene was recovered and only 70 g. of ethylated naphthalene products obtained.

From different runs some 700 g. of ethyl-naphthalene was prepared and, along with it, was obtained a series of fractions doubtless representing poly-ethyl-naphthalenes. The fraction 260–280° at 4 mm. deposited crystals which, after two recrystallizations from benzene and one from acetic acid, melted sharply at 179°. The supposed poly-ethyl-naphthalenes are viscous oils showing bluish-red fluorescence. The study of these must be postponed.

It is believed that other unsaturated hydrocarbons such as propylene,

⁹ Roux, *Ann. chim. phys.*, [6] 12, 289 (1887).

¹⁰ Ref. 9, p. 306, note.

¹¹ Fischer and Schneider, "Ges. Abhand. zur Kenntnis der Kohle," 1917, Vol. 1, p. 227, through *C. A.*, 13, 3183 (1919).

¹² Niggemann, *op. cit.*, Ref. 11, pp. 255–8, through *C. A.*, 13, 3184 (1919).

butylene, etc., will react with benzene under the same general conditions and it is intended to take up the study of these in this Laboratory.

Summary.

1. By the aid of intensive stirring ethylene can be made to react with benzene in the presence of aluminum chloride so rapidly and completely that this becomes a practical method for the ethylation of benzene.

2. Naphthalene can be readily ethylated by heating it with poly-ethylbenzenes and aluminum chloride under intensive agitation.

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AN IMPROVED METHOD FOR PREPARING RAFFINOSE.¹

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Several methods have been proposed for the preparation of raffinose.² All these procedures, however, with the exception of the method of Hudson and Harding, as these authors have well pointed out, have many serious disadvantages. The latter method, while it is a decided improvement over all others, and gives fairly good results on very small lots, nevertheless has objectionable features when applied to the preparation of larger quantities of the sugar. Chief among these may be mentioned the tedious procedure in extracting the meal, the necessity of evaporating large quantities of water, due to the excessive dilution of the extract, and the quantity and cost of the reagents required. The following method overcomes these disadvantages and enables one to prepare relatively large quantities of this sugar by a convenient and economical process.

Five kg. of coarsely ground cotton-seed meal is thoroughly moistened with 2 liters of water and allowed to stand overnight. It is then loosely packed in a cylindrical percolator, and sufficient water added to saturate the meal and leave a stratum above it. When the liquid begins to run from the percolator, more menstruum is added, from time to time, until a sample of the percolate, after defecation with dry basic lead acetate, has an optical rotation of not more than 1 circular degree in a 2dcm. tube.³

¹ Published by the permission of the Director, U. S. Bureau of Standards.

² von Lippmann, "Die Chemie der Zuckerarten," Friedrich Viewig und Sohn, Braunschweig, 1904, 3rd ed., pp. 1627-1630. Zitkowsky, *Am. Sugar Ind.*, **12**, p. 324 (1910). Hudson and Harding, *THIS JOURNAL*, **36**, 2110 (1914).

³ As there are substances in the meal which are extracted much more slowly than the sugar, and which cause difficulty in the subsequent steps, as well as give an inferior product, it is essential to obtain a quite rapid percolation, consuming not more than 30 to 35 minutes; and it is not expedient to carry the extraction beyond where the optical rotation of the liquid is less than 1° in a 2dcm. tube.