oximes demanded by theory. The one obtained, probably the *anti* form, could not be transmuted by hydrogen chloride.

5. Further work is in progress in this Laboratory.

Iowa City, Iowa

[Contribution from the Chemical Laboratory of Northwestern University]

PYROLYSIS OF ALLYLANILINES

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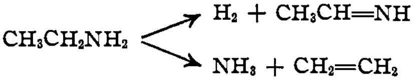
Allylaniline sufficiently resembles ethylamine and allyl phenyl ether in structure so that its pyrolysis may be considered to have points of similarity with theirs, both of which have been previously investigated. Primary effects of dehydrogenation and of deammonation have been shown to be the case[2] with ethylamine

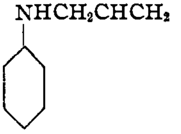


$$CH_3CH_2NH_2 \begin{cases} \rightarrow H_2 + CH_3CH{=}NH \\ \rightarrow NH_3 + CH_2{=}CH_2 \end{cases}$$

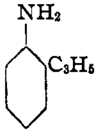
Most of the secondary reactions were traceable to the acetaldimide, chief of which was the further dehydrogenation into methyl cyanide or the demethanation into hydrogen cyanide.

For allylaniline to undergo the deammonation reaction the products would be aniline and allene. No allene was found in spite of careful search for it. The dehydrogenation reaction would give rise to acrolein-anil or its products of polymerization: $CH_2{=}CHCH_2NHC_6H_5 \longrightarrow H_2 + CH_2{=}CHCH{=}NC_6H_5$. Diallylaniline, $C_6H_5N(CH_2CH{=}CH_2)_2$, would give rise to acrolein-anil polymers by loss of propylene. Both of these reactions seem to occur. However, the fact that considerable aniline is formed during the pyrolysis of both mono- and di-allylaniline shows that this is not the exclusive feature.

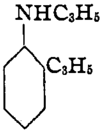
Allyl phenyl ether, on refluxing, has been shown to rearrange[3] into *o*-allylphenol. Similarly, N-allylaniline might be expected to change into *o*-allylaniline, and N,N-diallylaniline into either *o*-allylphenylallylamine or 2,6-diallylaniline. Inasmuch as pyrolysis of allyl phenyl ether gave rise



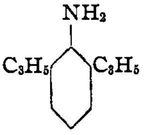
N-Allylaniline



o-Allylaniline



o-Allylphenyl-allylamine



2,6-Diallylaniline

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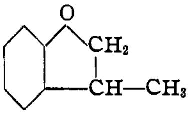
[1] Du Pont Fellow, 1929–1930.

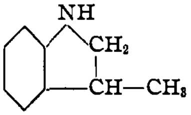
[2] Hurd and Carnahan, This Journal, **52**, 4151 (1930).

[3] For a discussion of this subject, see Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, **1929**, p. 215.

to a small yield of methylcoumaran in addition to the *o*-allylphenol, so it might be anticipated that N-allylaniline should give rise to methylindoline.



Methylcoumaran



Methylindoline

Preliminary study[4] of allyl- and diallylaniline indicated a pyrolysis on refluxing. The former changed partially into a primary amine, but it was not ascertained whether or not this was *o*-allylaniline. Similarly, the tertiary amine, diallylaniline, gave rise to both primary and secondary amines. Dains[5] found that the products obtained on heating allylaniline in a sealed tube at 250° for eight hours were unchanged amine, aniline, unsaturated gaseous hydrocarbons and a large amount of non-basic tarry material.

In this investigation it was established that the only primary amine formed from either allyl- or diallylaniline was aniline itself. It was further established that the secondary amine from diallylaniline was monoallylaniline and not *o*-allylphenylallylamine. Although diallylaniline is the ammono analog of allyl phenyl ether, and although both substances possess a similar instability, it is apparent that the final products of the reaction are not strictly comparable in the two cases; but this should not be interpreted to mean that no analogy exists. Diallyl-*p*-phenetidine, $C_2H_5O\text{-}C_6H_4\text{-}N(C_3H_5)_2$, was studied and its pyrolysis was found to be very similar to that of diallylaniline. Before discussing a mechanism of the pyrolysis, the general results will be outlined briefly.

General Discussion of Results

Propylene, in a fair state of purity, was liberated when either diallylaniline or diallyl-*p*-phenetidine was refluxed. It came more rapidly from the latter because of the higher reflux temperature (275°). Some diallylaniline was recoverable after two days of refluxing. Some allylaniline and larger amounts of aniline were isoluble. With diallylphenetidine, none was recoverable even when the reflux period had been shortened to two hours, nor was monoallylphenetidine found, but a large quantity of phenetidine was produced. In both cases over half of the original tertiary amine was changed into a non-volatile (at 23 mm. and 300°), brittle, black resin. The resin from diallylaniline possessed an average molecular weight of 783.

With monoallylaniline, the reflux temperature was too low for rapid pyrolysis. Accordingly, it was heated at 275° in a sealed tube. Aniline, gas and non-volatile tar were formed. When allylaniline vapor was

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[4] H. Greengard and C. D. Hurd, unpublished results.

[5] Dains, Brewster, Blair and Thompson, THIS JOURNAL, **44**, 2638 (1922).

passed through a pyrex tube at 600° at such a rate that a hot contact time of two and one-half minutes was maintained, a similar but more deep-seated pyrolysis occurred. A 14-g. sample gave nearly 5 g. of aniline, 2.3 g. of unidentified liquids, 0.5 g. of benzene, 2.3 g. of tar and 1.3 liters of gas (hydrogen, olefins and paraffins). None of the original allylaniline was recovered. A similar change occurred at 700° when the contact time was shortened to thirty-nine seconds. From a 50-g. sample the following substances were identified: 5.7 liters of gas, 4.5 g. of benzene, 19 g. of aniline, 1–2 g. of quinoline, 7.0 g. of other liquids and 8 g. of residue. The benzene which was produced in these high temperature experiments undoubtedly was formed by the splitting action of hydrogen on aniline (or aniline derivatives), an effect which has been previously established.[6]

The moles of the more important reaction products have been summarized in Table I.

Table I

Moles of Reaction Products Formed

Amine used	Moles taken	Moles converted into tar	Substances formed, moles			
			Propylene	Aniline or phenetidine	Allylaniline	Benzene
Diallylaniline (reflux)	0.146	0.104	0.038	0.035	0.011	...
Diallyl-*p*-phenetidine (reflux)	.138	.080	.062	.091	...	...
Allylaniline (reflux)	.044	.029	...	.011	...	...
600°	.105	.017	...	.054	...	0.007
700°	.376	.060	...	.204	...	.06

A preliminary study of acyl-allylanilines, C_6H_5N (allyl) (acyl), wherein the acyl group was acetyl and *p*-toluenesulfonyl.—Allylacetanilide, b. p. 149° at 24 mm., was prepared in 71% yield by the reaction of allylaniline and acetyl chloride in absolute ether. About two-fifths of it was recovered after four and one-half hours' heating at 300°. The remaining three-fifths was changed into higher-boiling material. Only a little gas was liberated. With allyl-*p*-toluenesulfonanilide, the decomposition at 300° was complex. Hydrogen sulfide was evolved and resin formation took place. Only traces of primary amine derivatives were formed in either case.

Mechanism of Pyrolysis of Allylanilines.—Resin formation may be accounted for through the intermediate acrolein-anil by the equations

$$\mathrm{Ar{-}NHC_3H_5} \longrightarrow \mathrm{H_2 + Ar{-}N{=}CH{-}CH{=}CH_2}$$
$$\mathrm{Ar{-}N(C_3H_5)_2} \longrightarrow \mathrm{C_3H_6 + Ar{-}N{=}CH{-}CH{=}CH_2}$$

No doubt these reactions do occur, and the presence of hydrogen from allylaniline provides an explanation for the presence of aniline: $\mathrm{ArNHC_3H_5 + 2H \longrightarrow ArNH_2 + C_3H_6}$. This is a reasonable equation for the 600 and 700° experiments, but a rather doubtful one for the others. However, aniline was formed generously in all cases. Furthermore, just as much aniline (and phenetidine) was formed when the diallyl derivatives

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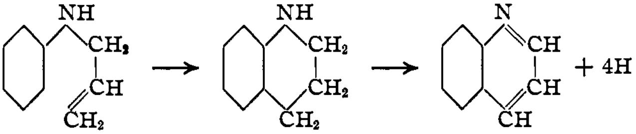
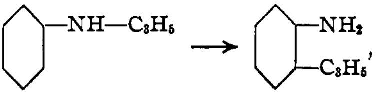
[6] Fischer and Schrader, *Brennstoff-Chem.*, **1**, 4, 22 (1920).

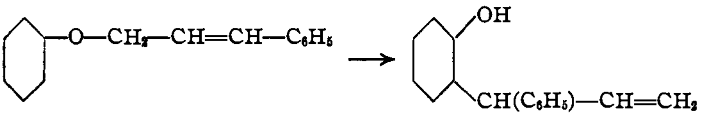
were heated as when monoallylaniline was taken, but the equation permits of no hydrogen formation with the diallyl derivatives. Aniline (or phenetidine) was not formed by direct cleavage, since allene was not formed.

Although allyl phenyl ether is known to pyrolyze into *o*-allylphenol, the ammono analogs in this case appear not to behave in a parallel manner. Thus, N-allylaniline does not pyrolyze into *o*-allylaniline. However, a carbon-to-carbon union at the ortho position was demonstrated in the 700° experiments with the isolation of quinoline. The following plan suggests itself to explain its presence

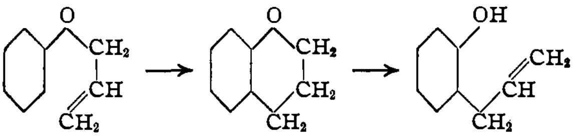


Such a series of reactions may seem to have little in common with the rearrangement  , which was discussed above.

However, it is important to note that it is the third carbon from the N which becomes attached to the ortho nuclear carbon. As Claisen[7] has demonstrated, such is also the case in allyl aryl ethers, as witnessed by the equation



The mechanism for such a rearrangement is speculative, but it is conceivable that it proceeds through a 6-membered oxygen ring. To illustrate with allyl phenyl ether



Quinoline, from allylaniline, may be explained in another fashion by assuming rearrangement to *o*-allylaniline, isomerization to 2-methylindoline, dehydrogenation to 2-methylindole, and rearrangement[8] to quinoline. Unidentified bases which may have contained tetrahydroquinoline, 2-methylindoline or 2-methylindole were produced in all experiments.

No single reaction seems adequate to explain the complex picture which this subject presents. It seems, however, that there are at least two major

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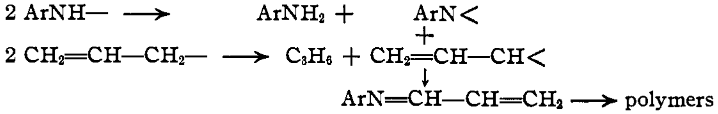
[7] Claisen and Tietze, *Ber.*, **58**, 275 (1925).

[8] The rearrangement of 2-methylindole into quinoline by passing it through a hot tube has been reported by Pictet, *Ber.*, **38**, 1949 (1905).

effects. One is the reaction of ring closure, giving bicyclic products. Fundamentally this seems related to the pyrolysis of allyl aryl ethers. The other effect is one which is caused by the loose type of union between the allyl radical and the nitrogen. It is convenient to picture this reaction as

$$\mathrm{Ar{-}NH{-}C_3H_5} \longrightarrow \mathrm{ArNH{-}} + \mathrm{{-}CH_2{-}CH{=}CH_2}$$

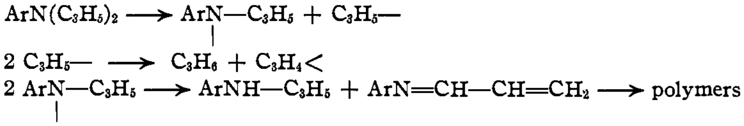
after which the radicals should disproportionate



$$\begin{array}{lcl} 2\,\mathrm{ArNH{-}} & \longrightarrow & \mathrm{ArNH_2} + \mathrm{ArN}< \\ & & \qquad\qquad\;\; + \\ 2\,\mathrm{CH_2{=}CH{-}CH_2{-}} & \longrightarrow & \mathrm{C_3H_6} + \mathrm{CH_2{=}CH{-}CH}< \\ & & \qquad\qquad\;\; \downarrow \\ & & \mathrm{ArN{=}CH{-}CH{=}CH_2} \longrightarrow \text{polymers} \end{array}$$

Propylene, aniline and resins are thus accounted for.

A similar situation would prevail with diallylaniline or diallyl-*p*-phenetidine



$$\begin{array}{l} \mathrm{ArN(C_3H_5)_2} \longrightarrow \mathrm{Ar}\underset{|}{\mathrm{N}}\mathrm{{-}C_3H_5} + \mathrm{C_3H_5{-}} \\ 2\,\mathrm{C_3H_5{-}} \longrightarrow \mathrm{C_3H_6} + \mathrm{C_3H_4}< \\ 2\,\mathrm{Ar}\underset{|}{\mathrm{N}}\mathrm{{-}C_3H_5} \longrightarrow \mathrm{ArNH{-}C_3H_5} + \mathrm{ArN{=}CH{-}CH{=}CH_2} \longrightarrow \text{polymers} \end{array}$$

This mechanism calls for allylaniline as an intermediate product. Some was isolated from diallylaniline, but for the most part it suffers further pyrolysis as outlined above.

The polymeric material with an average molecular weight of 783 may represent $(\mathrm{C_6H_5N{=}CHCH{=}CH_2})_6$, which has a molecular weight of 786. To ascertain whether the polymerization reaction was justified, acrolein and aniline were made to interact at 10°. A yellow resinous solid was formed which melted at about 76°. On heating, it changed into higher-melting resins which resembled those derived from the allylanilines. The reactivity of such anils is also evidenced in ethylidene-aniline, $\mathrm{C_6H_5N{=}CHCH_3}$, which is known[9] to change into 1,3-dianilino-1-butene at 10°. The resins from the pyrolysis of diallylaniline were similar but not identical in appearance with the material from acrolein and aniline. This would be expected, however, in view of the presence of such radicals as $\mathrm{C_3H_4}$, etc., with which the acrolein-anil could also unite.

Experimental Part

General Method of Investigation of Pyrolytic Products.—The mixtures obtained from the action of heat on allylanilines were subjected to fractional distillation first at atmospheric pressure and then under diminished pressure until only very high-boiling resinous material remained in the flask. The intermediate cuts in which were found the anilines were treated with *p*-toluenesulfonyl chloride in the presence of an excess of 10% potassium hydroxide solution. After standing for several hours the mix-

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[9] Von Miller, Plochl and Eckstein, *Ber.*, **25**, 2030 (1892).

ture was acidified and from the precipitated material was separated the derivative of the primary amine by solution in boiling 10% alkali in the usual way. The alkali-insoluble material was treated with sodium ethoxide to convert any disulfonyl derivatives of primary amines to the monosulfonyl ones. The *p*-toluenesulfonyl derivatives were, in general, purified by crystallization from methanol and water. Filter charcoal was used if necessary. The yields obtained from known quantities of the amines concerned were considered in determining the composition of mixtures by this plan.

Allylaniline

Synthesis.—Allylaniline was prepared in yields of about 30% by the action of allyl bromide on sodium acetanilide. After subsequent hydrolysis, the product was purified by vacuum distillation. Its boiling point was 115° at 23 mm. and 218° at 745 mm. The material contained about 2% of aniline by analysis. It was not found practicable to form allylaniline by the action of equimolar quantities of aniline and allyl bromide as Schiff[10] recommended.

Pyrolysis at 275°.—A sample of material containing 12.15 g. of allylaniline and 0.35 g. of aniline was heated in a sealed tube at 275° for twelve hours. A small amount of inflammable gas was noticed when the tube was opened. Distillation at atmospheric pressure gave 2.5 g. at 186–206°, 3.0 g. at 206–220°, 2.5 g. at 220–223° and a residue of 3.9 g. of black, viscid tar, not volatile even under reduced pressure. The three fractions were treated separately with *p*-toluenesulfonyl chloride and excess alkali. The presence in them of 1.38 g. of aniline and 6.24 g. of allylaniline was established. The identity of the derivatives obtained was verified in each case by the melting point and a mixed melting point with authentic specimens. The aniline derivative melted at 103° and its melting point was not lowered by admixture of known *p*-toluenesulfonanilide. Allyl-*p*-toluenesulfonanilide melted at 69° and a mixed m. p. had the same value.

Pyrolysis at 600°.—Allylaniline was dropped very slowly into a 50-cc. distilling flask held at 270°. The vapor thus formed was conducted through a horizontal pyrex tube heated to 600° in a gas combustion furnace. The temperature, as indicated by a chromel–alumel thermocouple potentiometer set-up, did not vary from this temperature by more than three degrees. A bent piece of smaller tubing, sealed to the exit end of the reaction tube, extended into a 25-cc. distilling flask. The latter was cooled in an ice–salt bath. A U-tube, in series with the flask and held at the same temperature, collected nothing. The residual gas was collected over water in a 2.5-liter bottle.

A 14-g. sample of allylaniline was passed through the apparatus in three hundred and fifty minutes. The dimensions of the tube and the barometric pressure were such that the contact time in the hot zone was 154 seconds. The amount of liquid product was 10.1 g. The gas collected was about 1300 cc. (0°, 760 mm.). It gave on analysis in percentage by volume: propylene 28.1, ethylene 12.9, hydrogen 9.4, carbon monoxide 2.8, paraffins 36.2 (n in C_nH_{2n+2} was 1.68), nitrogen 11.6. As would be expected under these conditions, much of the propylene which was formed underwent pyrolysis. Considerable carbonization and the presence of hydrogen cyanide in the off-gases were indicative of secondary reactions. Hydrogen cyanide was tested for by passing the gas through water in a test-tube and converting it into Prussian blue. Thus, alkali was added, then ferrous and ferric ions. On boiling for a minute and then acidifying, the blue precipitate appeared.

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[10] Schiff, *Ann. Supplement*, **3**, 364 (1864).

The liquid product was fractionated. Below 105° was obtained 0.5 g., which was presumably benzene. At 105–190° but mostly at 180–186° was collected 4.25 g. of liquid, 3.44 g. of which was confirmed as aniline through *p*-toluenesulfonanilide. Three grams of distillate containing 1.53 g. of aniline was collected at 120–150° and 70 mm. Summarizing, a sample of material containing 13.61 g. of allylaniline and 0.39 g. of aniline gave 4.97 g. of aniline, about 0.5 g. of benzene, 2.35 g. of non-distillable tar, and 2.28 g. of unidentified liquids. The 1300 cc. of gas contained propylene and its decomposition products. No unchanged allylaniline was found.

Pyrolysis at 700°.—During sixty-four minutes a 50-g. sample of allylaniline was displaced by mercury from a graduated capsule into a vertical pyrex tube. This tube was heated to 700° in an electric furnace whose temperature was automatically controlled and recorded by a Leeds–Northrup potentiometer type recorder-controller. The dimensions of the hot part of the reaction tube were 90 × 2.1 cm. and the contact time was calculated to be thirty-nine seconds. A small tube sealed to the main reaction tube passed into a 100-cc. distilling flask which was surrounded by an ice–salt bath. The products which condensed in this flask weighed 44 g. A U-tube in series with it and also cooled by ice–salt collected nothing. The gases of the reaction, collected over water at 21° and 740 mm., had a volume of 6.5 liters. The corrected volume was 5.7 liters.

The liquid product was fractionally distilled. The first fraction was collected at 740 mm. between 80–150°, mostly below 120°. This material was identified as benzene by conversion into *m*-dinitrobenzene, m. p. 87°; mixed m. p. 89°. The distillation was continued at 24 mm. The greater part of an 80–90° fraction weighing 19.7 g. came over at 87–88°. Of this, 15.7 g. was identified as aniline through conversion of a portion into *p*-toluenesulfonanilide. In the range of 90–200°, 11.5 g. of a deep yellow liquid was obtained; non-volatile residue, 8 g. Of the 11.5 g. of distillate, 3.4 g. was identified as aniline. Only a trace of secondary amine was present. The presence of 1–2 g. of quinoline in this fraction was established as follows. The tertiary amines in 2.27 g. of the distillate were separated, employing *p*-toluenesulfonyl chloride in the usual way. After steam distillation, ether extraction and evaporation of the ether, methyl iodide was added and the mixture allowed to stand for two to three hours. The solid obtained was crystallized from 3 cc. of absolute alcohol. The yellow crystals were pressed on a porous plate. They melted at 73°, the melting point of quinolinium methiodide. The mixed melting point with an authentic specimen was also 73°.

The analysis of the gas was as follows: CO_2, 0.7; unsatd. hydrocarbons soluble in 62.5% H_2SO_4, 1.3; propylene, 24.0; ethylene, 18.1; oxygen (from admixed air), 4.9; hydrogen, 15.9; CO, 0.6; residue of paraffins and nitrogen, 34.5.

Allyl-*p*-toluenesulfonanilide.—Allylaniline was treated with 1.5 equivalents of *p*-toluenesulfonyl chloride and 4–5 equivalents of 2 *N* potassium hydroxide. The mixture was allowed to stand overnight, acidified and worked up in the usual way. The yield was 75% and the melting point was 69°, or 69.3° corrected. An identical product was obtained in 89% yields by the action of an excess of allyl bromide on *p*-toluenesulfonanilide in *N* alkali solution. This method is preferable because of the difficulty in obtaining allylaniline. Unused *p*-toluenesulfonanilide was removed by solution in hot 2 *N* potassium hydroxide solution.

Anal. (Kjeldahl). Subs., 0.5155, 0.5437, 0.5329: cc. of 0.1311 *N* HCl, 13.68, 14.38, 14.00. Calcd. for $C_{16}H_{17}O_2NS$: N, 4.88. Found: N, 4.87, 4.83, 4.83.

Diallylaniline

Preparation.—This was prepared in 68% yield by the action of allyl bromide on residues from the attempted direct preparation of allylaniline. The boiling point of the nearly colorless liquid was 239–240° at 746 mm., 148° at 45 mm. and 123° at 18 mm. Its index of refraction, n_D^{23}, was 1.5556. It gave tests for only a trace of secondary amine and contained no primary amine.

Pyrolysis by Refluxing.—A 30-g. sample of diallylaniline was placed in a 100-cc. long-necked round-bottomed pyrex flask to which was sealed a piece of tubing 1 cm. in diameter and 60 cm. long to serve as an air condenser. A thermometer rested on the bottom of the flask and extended into the condenser. The flask was heated in a fused salt bath which was maintained at about 255°. With a reflux maintained at about 25 cm. above the liquid level, the temperature fell from the initial value of 240° to 228.5° in forty-eight hours.

About one liter of gas was evolved. Analysis showed the presence of 0.5% of carbon dioxide, 86.1 propylene, 0.5 ethylene, 0.7 oxygen, 3.4 hydrogen, 1.0 carbon monoxide, 3.4 paraffins (n in C_nH_{2n+2} was 1.7) and 4.4% of nitrogen. The identification of the main portion of the gas as propylene rather than allene was made in another run (40 g.) in which the gas evolved was passed into a solution of 18 g. of dry bromine in 200 cc. of dry carbon tetrachloride. The material which remained after removal of excess bromine and solvent was distilled at 50 mm. The main fraction (4 g.) boiled at 68–70°. This boiling point is much lower than that of allene tetrabromide, which[11] is 115.5° at 9 mm. The index of refraction gave confirmatory evidence that it was propylene bromide. At 23.5° the value was 1.5178 as compared to the known value at 20° of 1.5182. Two or three drops of higher-boiling material had an index at 23° of 1.5420 and the same amount of residue in the flask had one of 1.5720. The value for allene tetrabromide is 1.6200 at 20°. If the latter compound was not completely absent, it was certainly present in no more than traces.

After forty-eight hours' refluxing, the hot, sticky product was transferred as completely as possible to a Claisen flask equipped with a 20-cm. Vigreux column. The first fraction came over at 180–200° (atm. press.). Continuing at 23 mm., the next was collected from 100–123° and the third at 123°, constantly. The fractions weighed 2.8, 3.78 and 2.92 g., respectively. No more distillate could be obtained even when the flask was heated to 300° (23 mm.). While still hot, the residue was poured onto a watch glass. It solidified to form a brittle, black, resinous mass, weighing 18 g.

The three liquid fractions, with a total weight of 9.5 g., were separately treated with *p*-toluenesulfonyl chloride and alkali in the usual manner. The presence in them of 3.33 g. of aniline and 1.47 g. of allylaniline was established. The remainder was probably unchanged diallylaniline, to a certain extent. The identity of the derivatives with known samples was confirmed in each case.

Some work was done on the resinous material. About one-tenth of it was soluble in boiling 4 *N* hydrochloric acid. Neither the soluble nor the insoluble portion seemed to give quinones on oxidation with dichromate in dilute sulfuric acid solution. The molecular weight of the original resin in acetone was 783, an average of the values obtained from the following data.

Mol. wt. Subs., 2.1868 g.: vol. acetone taken, 26.0, 25.0, 26.5 cc.; ΔT, 0.255, 0.250, 0.235°. Mol. wts.: found, 793, 777, 779.

Action of Acrolein on Aniline.—To a solution of 9.3 g. of aniline in 10 cc. of 95% alcohol and held at about 10° in an ice-bath, there was added slowly the theoretical amount (5.5 g.) of acrolein. The reaction was strongly exothermic, giving a slightly yellow, sticky mass. This was washed with petroleum ether, then dissolved in ether and precipitated from it by the addition of petroleum ether. The solvent was poured off, and as the solvent evaporated from the residue, the sticky mass gradually changed into

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[11] Hurd, Meinert and Spence, THIS JOURNAL, **52**, 1145 (1930).

a slightly yellow powder. It started to soften and become dark colored at 68°, and melted at about 76°. Some of this material was heated at 150° for ten minutes. After cooling and solidifying, it then melted at 87°. This resin resembled in appearance the one which was formed in the pyrolysis of diallylaniline.

Diallyl-*p*-phenetidine

Synthesis.—To 50 g. of *p*-phenetidine in a balloon flask equipped with an air condenser was added 45 g. of allyl bromide in small portions. After being heated for fifteeen minutes on a water-bath, the mixture was made alkaline and extracted with ether. The solvent was evaporated from the dried ether extract and to the residue was added another 45-g. portion of allyl bromide. The mixture was heated on a boiling water-bath for fifteen minutes and allowed to stand overnight. It was made alkaline and ether-extracted. The extract was dried over stick potassium hydroxide, the ether evaporated and the residue distilled from a modified Claisen flask at 23 mm. The distillate boiling at 162–170° was 60 g., or 76% of the caculated amount. Redistillation gave 50 g. of pure material boiling at 164–165°. Its density, d_4^{23}, was 0.9921, and its index of refraction, n_D^{22}, 1.5458.

Anal. (Kjeldahl). Subs., 0.3456, 0.3594: cc. of 0.1311 *N* HCl, 12.46, 12.80. Calcd. for $C_{14}H_{19}ON$: N, 6.45. Found: N, 6.62, 6.55.

Preparation of *p*-Toluenesulfone-*p*-phenetidide.—A mixture of 7.8 g. of *p*-phenetidine, 19 g. of *p*-toluenesulfonyl chloride and 100 cc. of 2 *N* potassium hydroxide was allowed to stand overnight and was worked up in the customary manner. The treatment with sodium ethoxide must not be omitted. Altogether, there was obtained 13.4 g. of product, an 81% yield. Crystallization from methanol, accompanied by treatment with bone black, gave beautiful colorless crystals, melting at 109° (110°, corr.).

Anal. Subs., 0.5244, 0.5381: cc. of 0.1311 *N* HCl, 13.20, 14.04. Calcd. for $C_{15}H_{17}O_3NS$: N, 4.81. Found: N, 4.63, 4.80.

Pyrolysis of **Diallyl-*p*-phenetidine.**—A 30-g. sample of diallyl-*p*-phenetidine was heated in an all-glass apparatus in a fused salt bath. It refluxed at 265° with the evolution in seventeen minutes of 350 cc. of gas. Analysis showed this to be 95% propylene, 0.4% ethylene, 1.3% oxygen and 3.3% nitrogen. The remaining gas was led into 200 cc. of carbon tetrachloride which contained 18 g. of bromine. Identification of the major portion as propylene and not allene was accomplished as outlined above for the gas from diallylaniline. Distillation of the bromide derivative at 25 mm. gave 1.5 g. at 48–50°; its index of refraction was 1.5180. Practically complete distillation of the material remaining in the flask gave 1.75 g. with an index of 1.5225. The value for propylene dibromide at 20° is 1.5182, while that for allene tetrabromide is 1.6200. Furthermore, the boiling point of the latter compound is 115.5° at 9 mm., which is much higher than the value of the material in question.

After forty-four hours of refluxing, the hot contents of the reaction vessel were transferred to a modified Claisen flask and distilled at 25 mm. In the range of 139–146° there was obtained 7.9 g. of *p*-phenetidine, identified as *p*-toluenesulfone-*p*-phenetidide in a yield equivalent to that which was obtained from a sample of the pure amine. The melting point was 109° and this was unchanged by admixture of known material. Additional proof of the identity of the material as *p*-phenetidine was secured by diazotization, replacement by a cyanide group, and hydrolysis of the latter to *p*-ethoxybenzoic acid, m. p. 197°. From 146–165° was obtained 1.5 g., containing 0.9 g. of *p*-phenetidine. The brittle black resin which remained as a distillation residue weighed 17 g.

In brief, 30 g. of diallyl-*p*-phenetidine on refluxing at 276–272° for forty-four hours gave 8.8 g. of phenetidine, 1.35 g. of propylene (0.61 g. in 350 cc. of gas, and 0.74 g.

equivalent to 3.25 g. of the dibromide), 17 g. of resin, and 2.85 g. lost or unidentified. A weight of propylene that would be equivalent (2 moles) to the phenetidine formed would be 3.24 g. No monoallylphenetidine was found. Its stability at the reflux temperature of 275° is evidently less than that of allylaniline at 240°.

Pyrolysis. **Two Hours of Reflux.**—A 30-g. sample of diallyl-*p*-phenetidine on refluxing for two hours in an all-glass apparatus gave 10.6 g. of liquid products, 16.5 g. of resin and 2.65 g. of propylene. The phenetidine in the liquid products amounted to 8.07 g. These results are almost identical with those obtained with the forty-four hours reflux period. The greater recovery of propylene in this instance is due to the fact that the gas was collected as such and was not subjected to the unavoidable losses occasioned by its conversion into propylene dibromide.

Summary

The behavior of allylaniline, diallylaniline and diallyl-*p*-phenetidine at elevated temperatures has been studied. In general, the products are the parent primary amine, propylene and resinous material. Some quinoline was formed from allylaniline at 700°. Allene was not a product of the pyrolysis. Mechanisms have been suggested and discussed.

The following new compounds have been prepared and characterized: diallyl-*p*-phenetidine, allyl-*p*-toluenesulfonanilide and *p*-toluenesulfone-*p*-phenetidide.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. X. CLEAVAGE OF DERRITOL AND ROTENOL

BY L. E. SMITH AND F. B. LAFORGE

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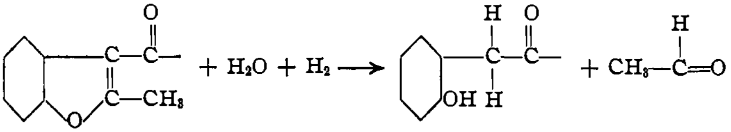
When rotenone, $C_{23}H_{22}O_6$, is boiled with zinc dust and potassium hydroxide in alcoholic solution, two products are obtained: derritol, a yellow phenol formed with the loss of two carbon atoms, and a white compound, rotenol,[1] which contains two hydrogen atoms more than rotenone and which exhibits the properties of an alcohol.

Butenandt[1] has advanced several theories to account for the formation of derritol of which the following mechanism is an example



Rotenone Derritol

Rotenol is assumed by the same author to be formed by the reduction of the carbonyl group of rotenone to a secondary alcohol group.

In previous articles[2,3] we have reported that several compounds derived

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[1] Butenandt, *Ann.*, **464**, 253 (1928).

[2] La Forge and Smith, THIS JOURNAL, **52**, 1091 (1930).

[3] La Forge and Smith, *ibid.*, **52**, 3603 (1930).