[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Decomposition of Allylanilines in the Presence of Zinc Chloride*

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In the decomposition at elevated temperatures of *N*-allylaniline in the presence of zinc chloride these products were isolated: *o*-allylaniline, *p*-propylaniline, hydrogen, propylene, tar. Comparably, *N*-cinnamylaniline and zinc chloride gave rise to *o*-cinnamylaniline, *p*-cinnamylaniline, 2-phenylquinoline, hydrogen, tar. A mechanism for these reactions and related Hofmann rearrangements is proposed. Several new compounds and new syntheses of old compounds are included.

Hofmann, in his classic study[2] of the pyrolysis of methylaniline hydrochloride, established that rearrangement into *p*-toluidine hydrochloride occurred on heating for a day at 350°. To explain this result he proposed thermal dissociation into aniline and methyl chloride, followed by their reaction to yield toluidine; but he sensed that any free methyl chloride should also give rise to tertiary and quaternary ammonium salts. In 1924, Howard and Derick[3] confirmed the essential accuracy of Hofmann's work. They reported rearrangement to begin at about the same temperature (300°) that quaternary salt formation was noticed.

Reilly and Hickinbottom[4] were engaged in a similar study in 1920, after which (1927–1935) a succession of papers appeared from Hickinbottom's laboratory.[5] In this work it was established that hydrobromides of *N*-alkylanilines may undergo thermal rearrangement to the *para* isomer accompanied by rearrangement of the wandering radical (as *N*-isobutylaniline to *p*-*t*-butylaniline), that olefins may accompany this change (as *N*-*n*-butylaniline to 2-butene), and that *N*-alkylanilines isomerize at elevated temperatures in the presence of metal halides as $ZnBr_2$ or $CoBr_2$ without rearrangement of the wandering radical (as *N*-isobutylaniline to *p*-isobutylaniline).

To gain further insight into this reaction *N*-allylaniline and *N*-cinnamylaniline were selected for study. Carnahan and Hurd[6] investigated the pyrolysis of *N*-allylaniline, finding as products aniline, propylene, and tar, but they used no zinc chloride or other acid during the heating.

In the present work it was found that a refluxing mixture of *N*-allylaniline and zinc chloride in xylene gave rise to *o*-allylaniline in 42% yield. No reaction occurred in refluxing benzene. At temperatures of 200–250° (no solvent) the products identified were aniline (35% yield), *p*-propylaniline (5-6% yield), gas (0.55 mole per mole of amine) which was 95% hydrogen and 3% propylene, and tarry products. Quinoline was not noticed.

N-Cinnamylaniline was treated similarly. Heating a mixture of it with zinc chloride and bromobenzene at 100° caused no change, but heating at 150° for 0.5 hr. yielded aniline, *o*-cinnamylaniline, 2-phenylquinoline, and a residue. It is noteworthy that no inversion of the cinnamyl group occurred in this process. A simple but apparently unreliable explanation for the formation of 2-phenylquinoline is cyclization of the *o*-cinnamylaniline, followed by dehydrogenation. Actually, however, no phenylquinoline was observed in the products from *o*-cinnamylaniline (150°, $ZnCl_2$, C_6H_5Br). Partial isomerization to *p*-cinnamylaniline, however, may have taken place.

When *N*-cinnamylaniline and zinc chloride were heated at 100° in toluene, aniline and 2-phenylquinoline were formed but no *o*-cinnamylaniline. About half of the *N*-cinnamylaniline was unchanged.

The major product from more drastic heating of zinc chloride and *N*-cinnamylaniline up to 250° was a red tar. Gas evolution, chiefly hydrogen, was brisk at 125–180°. Small amounts of aniline and 2-phenylquinoline were separable from the tar, but there was no *p*-(3-phenylpropyl)aniline. The latter would be analogous to *p*-propylaniline from *N*-allylaniline.

It will be noticed that our results resembled Hickinbottom's in that there was no isomerization or inversion of the wandering cinnamyl radical; thus, *o*- and *p*-cinnamylaniline from *N*-cinnamylaniline. This eliminates from consideration the intramolecular mechanism that is analogous to that which applies for the pyrolytic rearrangement of phenyl cinnamyl ether into *o*-(1-phenylallyl)phenol, and such a mechanism also is made unreasonable by two other facts. One fact is that it would not apply to the rearrangement of the saturated, wandering alkyl groups such as isobutyl in *N*-isobutylaniline. Secondly, a concerted mechanism of this type requires activation of the ortho nuclear position. This does obtain in the allyl ethers (I) but it cannot occur in the amine salts (II) because no

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(1) Standard Oil Company (Ind.) Fellow, 1948–1949.

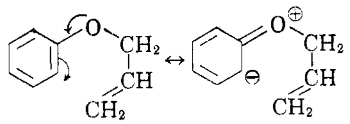
(2) A. W. Hofmann and C. A. Martius, *Ber.*, **4**, 742 (1871); A. W. Hofmann, *Ber.*, **5**, 720 (1872).

(3) J. W. Howard and C. G. Derick, *J. Am. Chem. Soc.*, **46**, 166 (1924).

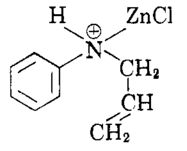
(4) J. Reilly and W. A. Hickinbottom, *J. Chem. Soc.*, **117**, 128 (1920).

(5) W. A. Hickinbottom and collaborators, *J. Chem. Soc.*, 64 (1927); 1558, 1566 (1930); 1281 (1931); 1700 (1934).

(6) F. L. Carnahan and C. D. Hurd, *J. Am. Chem. Soc.*, **52**, 4586 (1930).



I

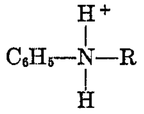


II

unshared electrons are available on the nitrogen to contribute to the resonance. Also, it is well known that a positive group deactivates the ortho and para positions.

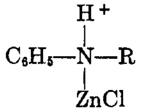
Hickinbottom[5] postulated a carbonium intermediate to explain the rearrangement of *N*-alkylanilines in the presence of metal halides, followed "by reaction of the positive alkyl 'ion' with the aniline nucleus reacting in the quinonoid form." To account for retention of structure of the wandering group he stated that "the expelled 'ion', in general, suffers no internal rearrangement, either on account of the stabilizing effect of the metal salt or because its reaction with the nucleus is catalyzed by the metal salt." This hypothesis would seem adequate to care for the rearrangement of *N*-isobutylaniline hydrobromide into *p*-*t*-butylaniline hydrobromide in view of what is known today of the facile hydrogen transfer found in the change of *i*-butyl carbonium into *t*-butyl carbonium. The latter either could alkylate the aniline nucleus or change into isobutylene by loss of a proton. It seems quite improbable, however, that a metallic salt such as zinc chloride should stabilize *i*-butyl carbonium against rearrangement into *t*-butyl. Hence, some other mechanism than the one proposed by Hickinbottom should be advanced to explain the rearrangements, in the presence of metal salts, which involve no isomerization of the wandering group.

The following mechanism is suggested. All previous workers have recognized that the rearrangement involves the salt and not the free amine, but the evidence shows that it makes a difference if the salt involves a strong acid such as hydrochloric (IIIa) or a mild Lewis acid such as zinc chloride (IIIb). It has been recognized also that the N-R



$$C_6H_5\text{—}\overset{H^+}{\underset{H}{N}}\text{—}R$$

IIIa



$$C_6H_5\text{—}\overset{H^+}{\underset{ZnCl}{N}}\text{—}R$$

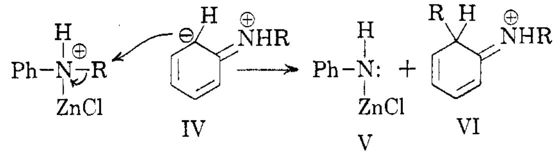
IIIb

bond in III is weaker than in the parent amine. Hofmann proposed dissociation into alkyl halide and Hickinbottom postulated cleavage into alkyl carbonium ion. In our opinion the bond is indeed weakened but not necessarily broken. We suggest that whereas the N-R bond in IIIa may be broken to yield a carbonium ion at sufficiently elevated temperatures, that in IIIb is not broken. Thus, in IIIa there are two competing dissociation reactions at elevated temperatures: $H^+ + C_6H_5NHR \rightleftarrows$ IIIa $\rightleftarrows R^+ + C_6H_5NH_2$. In IIIb, however, there is but one or, at least, the second is greatly minimized:

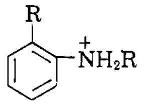
$$ClZn^+ + C_6H_5NHR \rightleftarrows \text{IIIb}.$$

Three features about this last equation stand out: (1) a weakened N-R bond in IIIb. (2) a nucleus in IIIb that is resistant to substitution because of low electron density at ortho and para positions. (3) a high electron density at ortho and para positions in the free amine, C_6H_5NHR (see IV).

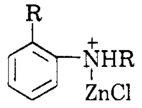
Finally, it is proposed that the basis of the rearrangement is attack of the weakened N-R bond of IIIb by the negative charge of IV:



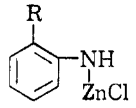
This mechanism calls for no separation of an alkyl carbonium ion, hence R would be attracted to the *ortho* or *para* position without inversion or isomerization. V is the precursor of aniline. VI tautomerizes to the substituted ammonium ion VIIa. Then: VIIa + V → $C_6H_5NH_2$ + VIIb, after which VIIb + IV → VIII (analogous to V) + VI. Eventually, the R groups become transferred from nitrogen to carbon.



VIIa



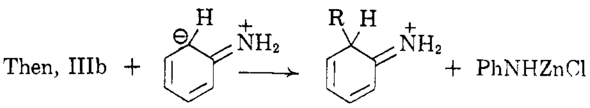
VIIb



VIII

This interpretation portrays VIII as coming from the original amine *via* VI and VII but one may also regard it as coming from aniline or V. To this end,

$$PhNH_2 + {}^+ZnCl \rightleftarrows Ph\overset{+}{N}H_2ZnCl \overset{PhNHR}{\rightleftarrows} PhNH_2 + \text{IIIb}.$$



Insufficient facts are at hand to offer a sound explanation for the formation of 2-phenylquinoline, especially in view of its non-formation from *o*-cinnamylaniline.

Another compound requiring explanation is the *p*-propylaniline from *N*-allylaniline at 200–250°. One may make the reasonable assumption that *p*-allylaniline is formed first, and that it becomes reduced to *p*-*n*-propylaniline by hydrogen abstraction from the other products which ultimately appear as tar. The evolution of hydrogen supports this viewpoint. It does not seem likely that propylene would be the precursor since then the product should be *p*-isopropylaniline. Hickinbottom[7] has

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(7) W. A. Hickinbottom, *J. Chem. Soc.*, 2396 (1932); 319, 1981 (1934); 1279 (1935).

reported that styrene, butadiene, and other olefins act towards aniline salts in this way.

Several new compounds were made and new syntheses developed in the course of this work. *N*-Allylaniline, formerly made by reaction of sodioformanilide[8] or sodioacetanilide[6] with allyl bromide or iodide, was prepared smoothly by reaction of allyl chloride and two parts of aniline.

An independent synthesis of *p*-propylaniline was developed from allylbenzene by hydrogenation, nitration to *p*-nitropropylbenzene, and reduction of the latter. Its derivative with phenyl isothiocyanate was prepared and found to melt at 119–120°, not 127–128° as was reported by Hickinbottom and Waine.[9] In a personal communication to us from Professor Hickinbottom, he accepts the lower value and believes that the value of 127–128° may have been an error in copying (for 117–118°).

o-Allylaniline and *p*-allylaniline, both new compounds, were made from allylbenzene by nitration to a separable mixture of *o*- and *p*-allylnitrobenzene. Reduction of these compounds to *o*- and *p*-allylaniline was by use of ferrous sulfate, boiling water, and ammonium hydroxide which was added gradually. Several solid derivatives of these amines were prepared. The structure of each allylaniline was proved by changing it to the corresponding, known allylphenol.

The synthesis of *o*-cinnamylaniline has not been previously described. It will be recalled that the synthesis selected for *o*-allylaniline started with nitration of allylbenzene, but a comparable synthesis from cinnamylbenzene would run the risk of nitration in the wrong aromatic nucleus. Hence, hydrocinnamic acid was taken as the starting point. After nitration to *o*-nitrohydrocinnamic acid, it was changed to the acyl chloride and then to ω-(*o*-nitrophenyl)propiophenone. The para isomer was also prepared in an identical manner.

These two ketones were prepared also from ω-phenylpropiophenone, but the separation of isomers was tedious and there was no improvement in the quality of the products.

The two nitro ketones were reduced to the corresponding nitro alcohols by use of aluminum isopropoxide, after which they were dehydrated to the *o*- and *p*-cinnamylnitrobenzenes. Ferrous sulfate again proved to be an efficient reducing agent for the nitro group without disturbing the olefinic group. In this way, *o*- and *p*-cinnamylaniline were prepared. Certain acyl derivatives of these amines were made for purposes of characterization.

EXPERIMENTAL

Preparation of reagents.

N-Allylaniline from allyl chloride. A mixture of 666 ml. of aniline and 296 g. of allyl chloride (some evolution of heat) was kept for 3 days at 25°, 8 hr. at 100°, then was cooled overnight. The solid mass of aniline hydrochloride was broken up, mixed with ether, collected, and rinsed with ether; yield 393 g., m.p. 192–193° dec. Titration with standard sodium hydroxide (phenolphthalein) demonstrated an equivalent weight of 127.5, 128.5 as compared to the calculated 129.6.

The filtrates were combined, washed twice with dilute sodium hydroxide, water, then dried (Na_2SO_4) and distilled. Diminished pressure was employed after the ether was removed, and these fractions were collected: (1) forerun, 202 g. (2) 88–96° (8 mm.), 232.5 g. (3) residue, 73 g. The residue, on distillation, yielded 15 g. of *N,N*-diallylaniline, b.p. 102–103.5° (8 mm.), n_D^{24} 1.5558. Carnahan and Hurd[6] reported b.p. 123° (18 mm.), n_D^{23} 1.5556.

Fraction 2 was redistilled. A 16-g. forerun was discarded, then 170 g. of *N*-allylaniline was collected at 93–95° (7 mm.), n_D^{20} 1.5636.

N-Cinnamylaniline. This compound was prepared by reaction of freshly distilled aniline in ether solution with freshly prepared cinamyl bromide, following the method of von Braun.[10] The fraction taken boiled at 159–160° at 1.2 mm.

N,N-Diallylanilinium picrate. Equivalent amounts of the amine and picric acid were mixed, both in benzene solution. Yellow crystals resulted which were collected and recrystallized from benzene; m.p. 122–122.8°.

Anal. Calcd. for $C_{18}H_{18}N_4O_7$: C, 53.74; H, 4.49. Found: C, 53.80; H, 4.50.

N-Allylaniline, on the other hand, formed no crystalline picrate when either benzene or ethanol were used as solvents.

o- and p-Nitroallylbenzenes. A nitrating solution was prepared of 58.5 ml. of fuming nitric acid (*d.* 1.5), 60 ml. of glacial acetic acid, and 47.5 ml. of acetic anhydride. The cold solution was added dropwise during 135 min. to a stirred solution of 110 g. of allylbenzene in 500 ml. of acetic anhydride. Temperature was maintained at 5–10° by cooling with an ice bath. The mixture then was poured onto 2.5 l. of ice, and after warming to room temperature and saturating with salt, the mixture was extracted with ether. Processing included ether extraction, washing, drying, distilling. After removing unreacted allylbenzene (35 g.), the nitro derivatives were collected at 94–105° (2 to 3 mm.). Redistillation gave a 29.5-g. fraction of *o*-nitroallylbenzene at 82–84° (1 mm.), n_D^{20} 1.5490, d_4^{20} 1.115.

Anal. Calcd. for $C_9H_9NO_2$: N, 8.58. Found: N, 8.55.

The fraction of *p*-nitroallylbenzene boiled at 89–94° at 1 mm. (5.2 g.). A center cut gave these constants: n_D^{20} 1.5532, d_4^{20} 1.112.

Anal. Calcd. for $C_9H_9NO_2$: N, 8.58. Found: N, 8.65.

Further evidence that this was *p*-nitroallylbenzene was its ready decolorization of bromine (in CCl_4), and by its oxidation to *p*-nitrobenzoic acid, m.p. 230–232°, with warm potassium permanganate solution.

o-Allylaniline. A solution of 286 g. of ferrous sulfate heptahydrate in 700 g. of water was brought to the boiling point and 23.7 g. of *o*-nitroallylbenzene was added. Then 200 ml. of concentrated ammonium hydroxide was added in small portions during 4.5 hr. Refluxing was maintained throughout. The mixture was filtered hot, and the precipitate and filtrate, after cooling, were washed thoroughly with ether. The washings were collected and extracted with dilute hydrochloric acid leaving 2.7 g. of original *o*-nitroallylbenzene. The acid extracts were washed once with ether, made alkaline, and extracted with ether. The extracts were combined, washed with water, dried, and the solvent distilled. The residue was fractionated. The *o*-allylaniline (10.6 g.) boiled at 99–100° at 8 mm ; n_D^{20} 1.5661, d_4^{20} 0.982.

Anal. Calcd. for $C_9H_{11}N$: N, 10.51. Found: N, 10.36.

Benzoylation, using benzoyl chloride and pyridine at 100° for 30 min., yielded *o*-allylbenzanilide, m.p. 122–122.5°.

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[8] F. B. Dains, R. Brewster, J. Blair, and W. Thompson, *J. Am. Chem. Soc.*, **44**, 2637 (1922).

[9] W. Hickinbottom and A. C. Waine, *J. Chem. Soc.*, **1930**, 1558.

[10] J. von Braun and L. Tauber, *Ann.*, **458**, 102 (1927).

The reported m.p. is 123–124°.[11] The following two new derivatives were prepared also.

o-Allylbenzenesulfonanilide. A mixture of 1.3 g. of *o*-allylaniline, 1.76 g. of benzenesulfonyl chloride, and 20 ml. of 10% sodium hydroxide was shaken vigorously for 10 min. and kept overnight. The mixture was diluted with water and washed with ether. The alkaline layer was acidified, warmed on the steam bath, cooled, and a poor yield of precipitate formed which was collected on the filter. The product was recrystallized from ethanol-water; m.p. 83.5–84°.

Anal. Calcd. for $C_{15}H_{15}NO_2S$: C, 65.90; H, 5.53. Found: C, 65.78; H, 5.64.

N-o-Allylphenyl-N'-phenylthiourea. This compound was prepared in good yield by addition of the amine to phenyl isothiocyanate. It was purified by crystallizations from ethanol, and melted at 115.2–115.4°.

Anal. Calcd. for $C_{16}H_{16}N_2S$: C, 71.60; H, 6.01. Found: C, 71.02; H, 5.89.

o-Allylphenol. A solution of 2.7 g. of *o*-allylaniline in 200 ml. of 4% aqueous sulfuric acid was prepared and chilled to −1°. A solution of 1.4 g. of sodium nitrite in 10 ml. of water was added slowly and with stirring. When addition was complete, a small amount of urea was added and the solution was gradually warmed to 25°. This dark solution was steam-distilled, the 700 ml. of distillate was extracted with ether, and the extract was washed several times with 10% aqueous sodium hydroxide solution. The alkaline extracts were washed once with ether, acidified with mineral acid, and extracted with ether. The ether solution was washed once with water, dried, and freed of solvent, and the residue was distilled *in vacuo*. The main fraction (0.9 g.) boiled at 100–105° at 11–12 mm. A forerun of 1.1 g. of material resembling allylbenzene was collected.

Reaction of this *o*-allylphenol with phenyl isocyanate, followed by several crystallizations from ligroin, yielded a derivative of m.p. 104.5–105°. For *o*-allylphenyl phenylcarbamate, Claisen and Eisleb[12] reported the m.p. of 106–106.5°.

p-Allylaniline. This reduction of *p*-nitroallylbenzene (5.1 g.) with ammoniacal ferrous sulfate followed the general procedure given for the *ortho* isomer, except that a steam distillation step was introduced rather than filtration to separate the product from the iron compounds. The yield of *p*-allylaniline was 1.95 g.; b.p. 98–102° at 15 mm.; n_D^{20} 1.5668, d_4^{20} 0.975.

Anal. Calcd. for $C_9H_{11}N$: N, 10.53. Found: N, 10.81.

These three new derivatives were prepared from *p*-allylaniline by reaction respectively, with benzoyl chloride and pyridine, with acetic anhydride, and with phenyl isothiocyanate: *p*-allylbenzanilide, m.p. 136–137° after crystallization from alcohol; *p*-allylacetanilide, m.p. 91–92°, from alcohol and water; N-*p*-allylphenyl-N'-phenylthiourea, m.p. 115.9–116° from alcohol.

Anal. of *p*-allylbenzanilide. Calcd. for $C_{16}H_{15}NO$: C, 81.00; H, 6.36. Found: C, 81.41; H, 6.46.

Anal. of *p*-allylacetanilide. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.39; H, 7.78.

Anal. of N-*p*-allylphenyl-N'-phenylthiourea. Calcd. for $C_{16}H_{16}N_2S$: C, 71.60; H, 6.01. Found: C, 71.53; H, 5.97.

p-Allylphenol. Four grams of *p*-allylaniline was mixed with 150 ml. of 8% aqueous sulfuric acid. The mixture was chilled to −2° and, while stirring, a solution of 2.07 g. of sodium nitrite in 10 g. of water was added slowly. After stirring for 1 hr. and adding a little urea, the mixture was warmed to 20° and steam distilled thereby collecting 500 ml. of distillate. The product was isolated in the same manner as *o*-allylphenol. The forerun (0.7 g.) possessed the odor of allylbenzene. The main product (1.72 g.) boiled at 105–110° at 11 mm. That this was *p*-allylphenol was confirmed by treating it with 3,5-dinitrobenzoyl chloride[13] to obtain the known *p*-allylphenyl 3,5-dinitrobenzoate, m.p. 103–103.5° (lit., 103.5–104°).

ω-(o-Nitrophenyl)propiophenone. Crude *o*-nitrohydrocinnamic acid, m.p. 107–110°, was prepared according to the method of Konek and Pacsu.[14] Its conversion into ω-(*o*-nitrophenyl)propiophenone, m.p. 68–69°, has been reported by Jaenisch[15] but with no experimental details.

We mixed 3.9 g. of the acid and 16 g. of thionyl chloride, refluxed the mixture for 90 min., removed the excess of thionyl chloride under reduced pressure, and dissolved the residual nitrohydrocinnamoyl chloride in 25 ml. of benzene. This solution was added dropwise during 20 min. into a stirred suspension of 3 g. of anhydrous aluminum chloride in 50 ml. of pure benzene. The mixture was stirred for 45 min. at 20°, 30 min. at 40°, and then was poured into 200 g. of cracked ice and water which contained 10 ml. of concd. hydrochloric acid. After several hours the mixture was extracted with ether and the combined extracts were washed with water, then with saturated sodium bicarbonate solution and dried, and the solvent was distilled. The residue weighed 5 g., m.p. 55–56°. The product was crystallized from 100 ml. of cyclohexane; yield, 3.5 g., m.p. 57–59°.

ω-(p-Nitrophenyl)propiophenone. This isomeric ketone was prepared in exactly the same manner as its *ortho* isomer. From 3.9 g. of crude *p*-nitrohydrocinnamic acid, m.p. 160–163°, there was obtained 6 g. of crude product. After crystallizing it from 50 ml. of methanol and drying, the purified product weighed 4 g. and melted at 99–100°.

Anal. Calcd. for $C_{15}H_{13}NO_3$: N, 5.49. Found: N, 5.40.

Direct nitration of ω-phenylpropiophenone. Cupric nitrate trihydrate (125 g.) was added in small portions during 90 min. to a stirred solution of 85 g. of ω-phenylpropiophenone[16] in 500 ml. of acetic anhydride that was kept at 20° by cooling. Then the mixture was stirred for 0.5 hr. at 20° and was poured into 2 l. of cracked ice and water. After several hours the product was collected on a filter, washed well with sodium bicarbonate solution and water, and air dried. The crude product (105 g.) was washed three times with 100-ml. portions of cold ether. The residue, when dried, weighed 70 g., m.p. 55–59° with softening at 53°.

Sixty grams of this mixture was washed twice with 200- and 100-ml. portions of ether. The residue, 21 g., melted at 94–96° and was crude *para* isomer. Recrystallization from methanol brought the m.p. to 99–100°; mixed m.p. with the *para* isomer prepared above, 99.5–100°. Evaporation of the ether from the filtrate gave about 40 g. of the crude ortho isomer, m.p. 55–58°. A 25-g. sample was crystallized from cyclohexane. The purified material (17.5 g. melted at 57–59° and a mixed m.p. with ω-(*o*-nitrophenyl)propiophenone was 57–59°. The material melting at 57–59° was used as such, but it was considered to be a constant melting mixture of the two isomers, composed chiefly of the ortho isomer.

1-Phenyl-3-o-nitrophenyl-1-propanol. Crude ω-(*o*-nitrophenyl)propiophenone, m.p. 57–59°, was reduced by the method of Meerwein, Ponndorf, and Verley as modified by Lund.[17] From 4 g. of the ketone there was obtained 4 g. of crude alcohol, m.p. 43–45°. One crystallization from benzene (25 ml.)-ligroin (100 ml.) gave 3.4 g. of product of m.p. 44.5–46°.

Anal. Calcd. for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.45. Found: C, 69.90, 70.00; H, 5.30, 5.88; N, 5.45.

1-Phenyl-3-p-nitrophenyl-1-propanol. This alcohol was prepared in the same manner as its *ortho* isomer. Four grams

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[11] J. von Braun and A. Steindorff, *Ber.*, **37**, 4726 (1904).

[12] L. Claisen and O. Eisleb, *Ann.*, **401**, 73 (1913).

[13] M. Phillips and G. Keenan, *J. Am. Chem. Soc.*, **53**, 1924 (1931); S. Palkin and R. Wells, *J. Am. Chem. Soc.*, **55**, 1556 (1933).

[14] F. Konek and E. Pacsu, *Ber.*, **51**, 855 (1918).

[15] A. Jaenisch, *Ber.*, **56**, 2448 (1923).

[16] This ketone was kindly supplied by G. D. Searle and Co., Skokie, Ill.

[17] A. L. Wilds, *Org. Reactions*, **II**, 178–223 (1944).

of ketone gave rise to 4 g. of crude alcohol, m.p. 111–112°. The product, after crystallization from 25 ml. of ethanol and drying, weighed 3 g.; m.p. 112–113°.

Anal. Calcd. for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.45. Found: C, 69.93; H, 5.92; N, 5.43.

o-Cinnamylnitrobenzene. A solution of 6.3 g. of 1-phenyl-3-*o*-nitrophenyl-1-propanol in 70 ml. of glacial acetic acid and 0.3 ml. of concentrated sulfuric acid was refluxed for 1 hr. and poured into 300 g. of cracked ice and water. After keeping it for 1 day, the product was collected on a filter and dried *in vacuo* over sodium hydroxide; yield, 6 g., m.p. 40–47°. The crude product was extracted with 150 ml. of boiling petroleum pentane, leaving a residue of 1–1.5 g. From the chilled extracts, 4 g. of product crystallized, m.p. 41–42.5°. Recrystallization from pentane brought the m.p. to 42–43°.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.29; H, 5.48; N, 5.86. Found: C, 75.33; H, 5.52; N, 5.83.

p-Cinnamylnitrobenzene. From 7.7 g. of 1-phenyl-3-*p*-nitrophenyl-1-propanol, treated identically, there was obtained 6.8 g. of crude product, m.p. 60–62°. After one recrystallization from 75 ml. of ligroin (b.p. 85–100°) using Darco, and a second crystallization from 50 ml. of ligroin, the pure product melted at 62–63°; yield, 4.3 g.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.29; H, 5.48; N, 5.86. Found: C, 75.55; H, 5.59; N, 5.79.

o-Cinnamylaniline. To a boiling suspension of 25.3 g. of crude *o*-cinnamylnitrobenzene, m.p. 37–46°, in 500 g. of water that contained 205.5 g. of ferrous sulfate heptahydrate was added 145 ml. of concd. ammonium hydroxide during a period of 0.5 hr. The mixture was stirred at reflux for 4 hr., then was filtered to remove the iron compounds. The details of processing followed closely those given above for *o*-allylaniline. The product boiled at 158–165° at 1 mm.; yield, 11.3 g. (51%). A crystalline picric salt could not be prepared in ethanol. These derivatives were made.

o-Cinnamylbenzanilide. One gram of *o*-cinnamylaniline was mixed with 0.7 g. of benzoyl chloride and 5 g. of pyridine. After 1 hr. at 100°, the mixture was poured into acidified water. An oil resulted which granulated quickly; yield, 1.3 g. One crystallization from 25 ml. of ethanol, with the filter aids Darco and Dicalite, gave 0.7 g. of product of m.p. 157–160°. A recrystallization gave the pure derivative, m.p. 160–160.5°.

Anal. Calcd. for $C_{22}H_{19}NO$: N, 4.47. Found: N, 4.43.

The filtrate from the crystallization contained 0.1 g. of *p*-cinnamylbenzanilide, m.p. 133–136°. This indicated that some of the *para* isomer had carried through in all the steps starting with *o*-nitrohydrocinnamic acid.

o-Cinnamylbenzenesulfonanilide. One gram of *o*-cinnamylaniline, 1 g. of benzenesulfonyl chloride, and 20 ml. of 10% aqueous sodium hydroxide were mixed and shaken for 5 min. with occasional cooling by tap water. An additional gram of the halide was added and the mixture was shaken and kept for about 1 hr. The alkali soluble material was then isolated in good yield. It was crystallized from ethanol; m.p. 130–131°.

Anal. Calcd. for $C_{21}H_{19}NO_2S$: N, 4.01; S, 9.18. Found: N, 3.98; S, 8.99.

p-Cinnamylaniline. This compound was prepared in the same manner as the *ortho* isomer. From 15 g. of *p*-nitrocinnamylbenzene was obtained 5 g. of the amine, b.p. 172–176° at 2 mm. The distillate solidified and melted at 53–55°. A crystalline picric salt could not be prepared in ethanol.

p-Cinnamylbenzanilide. The derivative was prepared in the same manner as its *ortho* isomer. The crude product formed in good yield but it was crystallized from ethanol with difficulty. The pure product was obtained in a microcrystalline state; m.p. 134–136°. The melting point was not altered by changing crystallizing solvents.

Anal. Calcd. for $C_{22}H_{19}NO$: N, 4.47. Found: N, 4.42.

PROPYLBENZENE, *p*-PROPYLANILINE AND ALLIED COMPOUNDS

Propylbenzene. This compound has been prepared by several methods in the past, but not by hydrogenation of allylbenzene. To this end, 35.4 g. of allylbenzene (b.p. 155–158°) was added to a suspension of 1 g. of 5% palladium-on-charcoal catalyst (Wilkins-Anderson Co.) in 150 ml. of glacial acetic acid. The mixture was hydrogenated in a low-pressure Parr hydrogenation apparatus until a pressure drop of 25.3 lbs. was observed. The catalyst was removed on a filter and the filtrate was chilled, neutralized with 40% aqueous sodium hydroxide, and extracted with ether. The combined extracts were washed with water, dried, and distilled. The desired product (28.1 g.) boiled at 157–158.5°.

Nitration. To a mixture of 37 g. of propylbenzene in 165 ml. of acetic anhydride was added a nitrating solution at 0° to −5° during 80 min. [19.2 ml. of fuming nitric acid (*d.* 1.5), 15.6 ml. of acetic anhydride, 18 ml. of glacial acetic acid]. After treatment with crushed ice, alkaline washes, and drying 25 g. of *o*-nitropropylbenzene was collected at 115–122° (13 mm.) and 6.3 g. of *p*-nitropropylbenzene at 132–140° (13 mm.). Baddeley and Kenner reported[18] 133–140° and 150–160° at 20 mm., respectively. They used a nitric-sulfuric nitrating mixture.

p-Propylaniline. A suspension of 0.15 g. of 5% palladium-on-charcoal catalyst in 75 ml. of ethanol and 6.25 g. of *p*-nitropropylbenzene was hydrogenated in the low pressure Parr machine. Hydrogenation ceased when a pressure drop of 7 lbs. was observed. The catalyst was removed, and after adding 6 ml. of concd. hydrochloric acid to the filtrate the solvent was distilled off under reduced pressure. The solid residue was dissolved in water and the solution was made alkaline and ether extracted. The extracts were washed with water and dried, the solvent was removed, and the residue was distilled. The main fraction (2.35 g.) boiled at 102–105° at 11–12 mm. Baddeley and Kenner's value[18] was 112° (20 mm.). Benzoylation yielded a crystalline product, m.p. 118–119°, comparing with the known[19] benzo-*p*-propylanilide.

Derivatives of p-propylaniline. N-p-Propylphenyl-N′-phenylthiourea. *p*-Propylaniline, b.p. 103–105° (12 mm.), was treated with phenyl isothiocyanate. The crude product, obtained in high yield, was crystallized three times from ethanol; m.p. 119.1–119.2°. See ref. 9.

Anal. Calcd. for $C_{16}H_{18}N_2S$: C, 71.06; H, 6.70. Found: C, 71.20; H, 6.87.

Reaction of N-allylaniline with zinc chloride. At 140°. *N*-Allylaniline (13.3 g.), 13.6 g. of powdered, anhydrous zinc chloride and 30 ml. of xylene were mixed and refluxed for 3 hr., then left overnight and cooled in an ice bath while enough 40% sodium hydroxide aqueous sodium hydroxide was added to dissolve the initially precipitated zinc hydroxide. The xylene layer was separated, the alkaline layer extracted three times with ether, and the extracts were combined with the xylene layer. The latter was washed once with water, dried (Na_2SO_4), and distilled. After removing the xylene, there was a forerun of 1.0 g. which boiled up to 119° at 28 mm. The main fraction of 5.2 g. was collected between 119–122.5° at 28 mm. The residue weighed about 3 g. and decomposed on attempted distillation.

The main fraction was *o*-allylaniline, obtained in 42% yield. Its identity was certified by changing it into these derivatives: *o*-allylbenzanilide, m.p. and mixed m.p. 121–122°; *N*-*o*-allylphenyl-*N*′-phenylthiourea, m.p. and mixed m.p. 115–116°.

At reflux temperature. *N*-Allylaniline (100 g.) and 50 g. of zinc chloride were mixed in a flask fitted with an air condenser. The mixture was heated to boiling, when a vigorous reaction took place with gas evolution (see below). The mixture was refluxed for 2 hr. and, while still hot, was poured

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(18) G. Baddeley and J. Kenner, *J. Chem. Soc.* 303 (1935).

(19) G. Schultz, *Ber.*, 42, 3614 (1909), listed m.p. 115°; ref. 9 listed the m.p. as 116–117°.

into cold water, made alkaline (40% NaOH), and steam distilled. Three liters of distillate was collected during which time the alkaline suspension became purple in color. The material which did not distil was collected by decantation and weighed 40–45 g. when practically dry. This substance was a black tar possessing a fecal or skatole-like odor.

The distillate was saturated with salt, ether-extracted three times, and the extracts were washed with water, dried, and distilled. Fraction I was aniline (25.1 g., b.p. 64–70° at 7 mm., thiocarbanilide, m.p. 149–150°). Fraction II (3.8 g., b.p. 70–90° at 7 mm.) was the forerun to fraction III (9.3 g., b.p. 90–132° at 7 mm.). Fraction III, on redistillation, gave 6.4 g. (5–6% yield) of quite pure *p*-propylaniline, b.p. 102–105° (12 mm.). From it was made *N*-*p*-propylphenyl-*N'*-phenylthiourea, m.p. 119.9–120°; mixed m.p. with an authentic specimen, 119°. Benzo-*p*-propylanilide, m.p. 117–118°, also was prepared from this amine; mixed m.p., 117.5–118.6°.

Gas was collected from a similar, smaller run (*N*-allylaniline 25 g., $ZnCl_2$ 12.5 g.) in which the heating up to a final internal temperature of 300° was conducted in an atmosphere of carbon dioxide. Two liters of gas was evolved and was analyzed in a modified Orsat apparatus. The CO_2 content was 0.6 l. Traces of air and carbon monoxide comprised 0.03 l. Of the remaining 1.37 l. the composition was hydrogen 97.2%, olefin 2.8%. The olefin fraction was absorbed by 85% sulfuric acid, thus pointing to propylene[20] and excluding ethylene or acetylene.

In refluxing benzene. No product other than starting material (71% recovery) was found after 2 hr. refluxing of a mixture of 13.3 g. of *N*-allylaniline, 13.6 g. of zinc chloride, and 50 ml. of benzene.

Reaction of N-cinnamylaniline with zinc chloride. At 150° in bromobenzene. A mixture of 52.5 g. of *N*-cinnamylaniline, 34 g. of pulverized, anhydrous zinc chloride, and 150 ml. of bromobenzene was warmed at 147–152° (internal temperature) with stirring for 30 min., then was cooled to 25° and 33% aqueous sodium hydroxide was added until all of the zinc hydroxide dissolved. The mixture was extracted with ether and the combined ether layers were extracted thoroughly with dilute hydrochloric acid. The acidic extract was made alkaline and the base was isolated by ether-extraction. The extract was washed with water, dried, and distilled under diminished pressure. The forerun was aniline (8. g.); it yielded benzanilide as derivative (1.5 g. from 1 g.), m.p. and mixed m.p. 161–162°.

The main fraction weighed 17 g. There was a residue of 14 g. which was not processed. The 17-g. fraction, b.p. 168–184° at 1 mm., yielded 14 g. on redistillation, b.p. 172–174° at 1 mm. As shown below, half of it was *o*-cinnamylaniline and about 35–40% of it was 2-phenylquinoline. The latter was characterized by way of its insoluble picrate,[21] m.p. and mixed m.p. 186–188°, that was obtained by mixing hot alcoholic solutions of the base and picric acid.

A 2-g. portion of the 14-g. fraction was treated with 2 g. of benzenesulfonyl chloride and an excess of dilute sodium hydroxide solution. This yielded 0.70–0.75 g. (35–38%) of insoluble 2-phenylquinoline, and a soluble fraction that contained 0.85 g. of crude *o*-cinnamylbenzenesulfonanilide which precipitated on acidification. After 3 crystallizations from alcohol the latter melted at 128–128.5°; mixed m.p. with authentic sample (130–131°), 128.5–130°.

A 1-g. portion of the 14-g. fraction, treated with benzoyl chloride and pyridine for an hour at 100°, yielded 0.6 g. (40%) of a benzoyl derivative. After two crystallizations from alcohol, it melted at 159.5–160° and analysis showed 4.4% nitrogen, which is correct for $C_{22}H_{19}NO$. A mixed m.p. with authentic *o*-cinnamylbenzanilide (160–160.5°) was 159.5–160°.

At 110° in toluene. The quantities in this run were 24.5 g. of *N*-cinnamylaniline, 15.8 g. of zinc chloride, and 150 ml. of toluene. The mixture was stirred at 110° for 2 hr., then was left 15 hr. before processing essentially as in the above run. The basic products, when distilled, contained aniline (3.9 g.), a main fraction at 168–175° (1 mm.) weighing 12.6 g., and a residue (6. g.). The main fraction was about four-fifths unchanged N-cinnamylaniline (alcohol-soluble picrate) and one-fifth 2-phenylquinoline (alcohol-insoluble picrate), and it was separated by way of the picrates.

That *o*-cinnamylaniline was absent was shown by testing with cold nitrous acid and then attempting diazo coupling with alkaline 2-naphthol; no azo dye resulted, hence no primary amine was present in significant amounts.

At 250°. No solvent was used, as 72 g. of *N*-cinnamylaniline and 38 g. of zinc chloride were heated in CO_2 atmosphere in a flask equipped for gas collection. At a bath temperature of 100° the mixture began to turn red, at 125° gas evolution commenced, and at 150° gas evolution was brisk. Reaction became exothermic and the internal temperature reached 228° (bath, 190°). The gas volume was about 300 cc. When reaction subsided, heating was continued. At 215° the mixture began to froth with moderate gas evolution, at 231° decomposition seemed to commence, and at 233° frothing was vigorous. The reaction was stopped at 250°. After sweeping the apparatus with carbon dioxide the total volume of gas collected was about 1350 cc. The reaction mixture, while hot, was poured into a liter of water.

That portion of the gas that was insoluble in caustic solution was 405 cc. (STP). This was 97% hydrogen and the rest was chiefly air and a trace of olefin.

From the reaction mixture was isolated 5 g. of aniline, 2.5 g. of 2-phenylquinoline, and a large amount of brilliant red tar that was insoluble in acids, alkali, or ether. No *o*-cinnamylaniline remained, but if the heating was stopped at 150° then some was observed and identified as the benzenesulfonyl derivative, m.p. 130–131°.

Reaction of o-Cinnamylaniline with zinc chloride at 150°. No gas was liberated when a mixture of 4.5 g. of *o*-cinnamylaniline (containing some para isomer), 3.5 g. of anhydrous, powdered zinc chloride, and 20 ml. of bromobenzene was warmed at 150° for 30 min. The mixture was cooled to room temperature and 75 ml. of 33% sodium hydroxide solution was added. The basic material was processed as in other runs. It weighed about 2.8 g., b.p. 152–155° at 0.8 mm. with only about 0.5 g. of residue. The distillate partially solidified and a sample, dried on unglazed porcelain, melted at 52–54°. A mixed m.p. with *p*-cinnamylaniline (m.p. 53–55°) was 52–55°. One gram of distillate formed 1.5 g. of the crude, damp benzoyl derivative which, after two crystallizations from ethanol, melted at 120–131°. A mixed m.p. with a known mixture of *o*- and *p*-cinnamylbenzanilides (m.p. 119–121.5°) was 118–128°. If it is assumed that the material which was lost during the reaction was chiefly *o*-cinnamylaniline then the percentage of *para* isomer in the distillate would be raised since it was an original impurity.

Neither the distillate nor the residue formed a crystalline picrate in ethanol. This is the expected behavior for *o*- and *p*-cinnamylaniline, but not for a mixture containing any appreciable amount of 2-phenylquinoline.

The *ortho* isomer was identified by reaction of 1 g. of the above distillate with 2 g. of benzenesulfonyl chloride and 20 ml. of 10% aqueous sodium hydroxide. The crude yield of *o*-cinnamylbenzenesulfonamilide was 1.1 g. (64%). One crystallization from 4 ml. of ethanol gave the pure amide (0.6 g.), m.p. and mixed m.p. 130–131°.

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[20] C. D. Hurd and L. U. Spence, *J. Am. Chem. Soc.*, **51**, 3353 (1929).

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