

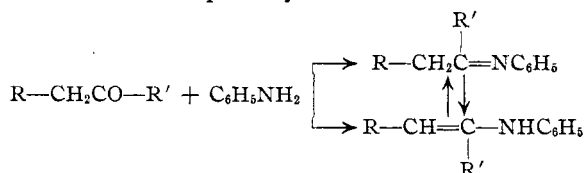
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Addition of Aryl Amines to Alkynes<sup>1</sup>

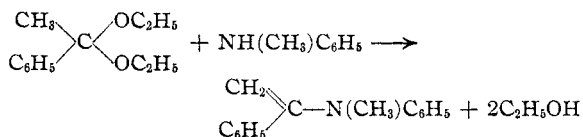
BY J. A. LORITSCH AND R. R. VOGT

## Introduction

The condensation of aryl amines with ketones to produce the anils by the elimination of water has been studied by several investigators.<sup>2-4</sup> A more feasible method of eliminating two molecules of an alcohol by the reaction of ketals and primary aryl amines has been reported.<sup>5,6</sup> The products derived from the primary amines usually have been written with a double bond between nitrogen and carbon. However, tautomerism is possible in the anils from primary amines.<sup>7-9</sup>

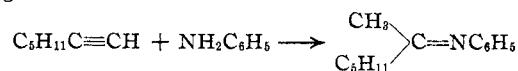


The anil structure is not possible in the compounds derived from secondary amines, which appear to have a double bond between two carbon atoms. N-Disubstituted ethylenic amines have been prepared from ketals and secondary aryl amines by the elimination of two molecules of an alcohol.<sup>10</sup>

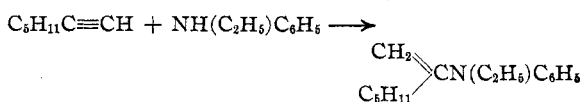


There is some evidence that ethylidene aniline ( $\text{CH}_3\text{CH}=\text{NC}_6\text{H}_5$ ) may be the primary product of the condensation of acetylene and aniline in the presence of mercuric halide.<sup>11</sup> However, the product usually isolated consists of diethylidene aniline ( $\text{C}_6\text{H}_5\text{NHCH}(\text{CH}_3)\text{CH}=\text{CHNHC}_6\text{H}_5$ ) or, at higher temperatures, of heterocyclic compounds such as indole and quinaldine.<sup>12,13</sup>

The present paper describes the condensation of aniline with 1-heptyne and 3-octyne, and of ethylaniline with 1-heptyne in the presence of mercuric oxide and boron fluoride. With the primary amine the chief product was the anil, *e. g.*



With the secondary amine, an N-disubstituted ethylenic amine was obtained, *e. g.*



A small quantity of a high-boiling oil was obtained in each experiment except with 3-octyne. Molecular weights and nitrogen percentages indicated that these by-products were derived from the condensation of two molecules of 1-heptyne with one molecule of the amine. Nitrogen analyses of the undistillable residues showed that these by-products must be unsaturated compounds capable of progressively adding molecules of the alkyne. The amount of unreacted alkyne recovered never exceeded 15% of the amount used, whereas the amine was recovered up to 50% of the theoretical amount.

Failure to obtain a reaction between diethylaniline and 1-heptyne appears to prove that substitution of the alkylidene group for the hydrogen of the benzene ring does not occur under these conditions.

## Experimental

**General Procedure.**—The same apparatus was used in all the experiments. It consisted of a 500-cc. three-necked flask equipped with a dropping funnel, a mercury-sealed stirrer, and a short spiral reflux condenser closed at the top by a calcium chloride tube.

The aryl amine was dried by heating with a small quantity of sodium or better by distilling over a little sodium. In the flask were placed 0.5–1 mole of the amine, 5–15 g. of mercuric oxide, and 2–6 g. of the ethyl ether boron fluoride compound. The mixture was warmed gently with stirring to ensure partial solution of the solid catalyst. One-half mole of the acetylenic hydrocarbon was then added from the dropping funnel at the rate of two drops per second, with constant stirring. In reactions of aniline the temperature rose spontaneously, but in reactions of ethylaniline it was found necessary to

(1) Paper No. XXXIV on the chemistry of substituted acetylenes; previous paper, *THIS JOURNAL*, **61**, 1460 (1939).

(2) Reddelien, *Ber.*, **53B**, 345, 355 (1920).

(3) Pauly, *Ann.*, **187**, 222 (1877).

(4) Riehm, *ibid.*, **238**, 1 (1887).

(5) Claisen, *Ber.*, **29**, 2923 (1896).

(6) Hoch, *Compt. rend.*, **199**, 1428 (1934).

(7) Von Auwers and Susemihl, *Ber.*, **63B**, 1072 (1930).

(8) *Idem.*, **64B**, 2748 (1931).

(9) Basu, *J. Indian Chem. Soc.*, **12**, 299 (1935).

(10) Hoch, *Compt. rend.*, **200**, 938 (1935).

(11) Kozlov and Mitskevich, *J. Gen. Chem.* (U. S. S. R.), **7**, 1082 (1937).

(12) Majuna, Unno and Ono, *Ber.*, **55B**, 3854 (1922).

(13) Kozlov and Golod, *J. Gen. Chem.* (U. S. S. R.), **6**, 1089 (1936).

supply heat. The temperature in all cases was maintained in the range 50–60° for about one hour, and was then allowed to fall to room temperature. At this point enough anhydrous potassium carbonate was added to destroy the boron fluoride compound. The reaction mixture was then filtered through cotton to remove free mercury, potassium carbonate, and other solids. Any unreacted acetylenic hydrocarbon was removed by distillation at atmospheric pressure, and the remaining product was fractionated at 4 mm. pressure, employing a 5-mm. glass-jacketed column, which was heated by a resistance wire.

An increase in the quantities of mercuric oxide and ether boron fluoride over the minimum amounts did not increase the yield. The use of equimolar proportions of aryl amine and acetylenic hydrocarbon appeared to give about as good yields as the use of excess aryl amine.

**Addition of Aniline to 1-Heptyne.**—Five experiments in which one mole of aniline and one-half mole of 1-heptyne were employed yielded 24 to 32 g. each of the anil, a light yellow oil which darkens rapidly on exposure to light and air, b. p. 88–90° at 4 mm.;  $d^{26}_4$  0.974.

*Anal.* Calcd. for  $C_{13}H_{19}N$ : C, 82.6; N, 7.4; mol. wt., 189. Found: C (wet combustion), 81.9; N, 7.5; mol. wt. (cryoscopic in benzene), 187.

The anil was further identified by hydrolyzing with dilute mineral acid to produce methyl amyl ketone and aniline.

There was also obtained 15 to 20 g. of a dark yellow oil, b. p. 138–41° at 4 mm.;  $d^{26}_4$  1.017.

*Anal.* Calcd. for  $C_{20}H_{33}N$ : C, 83.7; N, 4.87; mol. wt., 287. Found: C (wet combustion), 82.9; N, 4.53; mol. wt. (cryoscopic in benzene), 294.

**Addition of Ethylaniline to 1-Heptyne.**—Four experiments with half-mole quantities of 1-heptyne yielded 14 to 30 g. of the N-disubstituted ethylenic amine, a light yellow oil, b. p. 92–94° at 4 mm.;  $d^{26}_4$  0.949.

*Anal.* Calcd. for  $C_{15}H_{23}N$ : C, 82.9; N, 6.45; mol. wt., 217. Found: C (wet combustion), 82.3; N, 6.39; mol. wt. (cryoscopic in benzene), 214.

This compound hydrolyzed to amyl methyl ketone and ethylaniline.

From 3 to 10 g. of a by-product was isolated from each experiment, a dark yellow oil, b. p. 146–149° at 4 mm.;  $d^{26}_4$  0.967.

*Anal.* Calcd. for  $C_{22}H_{37}N$ : C, 83.8; N, 4.45; mol. wt., 315. Found: C (wet combustion), 82.9; N, 4.16; mol. wt. (cryoscopic in benzene), 325.

**Addition of Aniline to 3-Octyne.**—Two experiments with one mole of aniline and one-half mole of 3-octyne gave 18 to 19 g. of the anil, a light yellow oil, b. p. 95–97° at 4 mm.;  $d^{26}_4$  0.919.

*Anal.* Calcd. for  $C_{14}H_{21}N$ : C, 82.8; N, 6.9; mol. wt., 203. Found: C (wet combustion), 82.3; N, 6.8; mol. wt. (cryoscopic in benzene), 200.

The anil hydrolyzed to butyl propyl ketone and aniline with dilute mineral acid.

### Summary

The addition of aniline to 1-heptyne and 3-octyne, and of ethylaniline to 1-heptyne, in the presence of mercuric oxide and boron fluoride, gave fair yields of the anils and N-disubstituted ethylenic amine, respectively.

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## The Methylation of Aromatic Compounds by Methyl Ether-Boron Fluoride<sup>1</sup>

BY A. J. KOLKA AND R. R. VOGT

### Introduction

The replacement of hydrogen atoms linked to an aromatic ring by methyl groups usually has been accomplished by a Friedel-Crafts reaction using an aluminum halide catalyst with methyl halides,<sup>2</sup> methyl alcohol,<sup>3</sup> methyl sulfate<sup>4</sup> and methyl chlorocarbonate.<sup>5</sup> The Friedel-Crafts reaction leads to products in which one or several hydrogen atoms linked to an aromatic ring may be replaced by the methyl group. For this pur-

pose methyl bromide and iodide are rather expensive, and methyl chloride is difficult to handle under laboratory conditions.

The methylation of phenol with methyl alcohol in the presence of boron fluoride has been reported<sup>6</sup> and traces of the methylphenols and methyl phenyl ethers were obtained. Various ethers, other than methyl ether, in conjunction with boron fluoride have been used for alkylating benzene.<sup>7</sup>

The present paper describes preliminary work on the methylation of aromatic compounds by means of methyl ether-boron fluoride, and is concerned principally with the methylation of phenol

(1) Paper XXII on the reactions with boron fluoride; previous paper, in press.

(2) Jacobsen, *Ber.*, **14**, 2624 (1881); Friedel and Crafts, *Ann. chim.*, [6] **1**, 449 (1884).

(3) Tsukervanik and Vikhrova, *J. Gen. Chem.* (U. S. S. R.), **7**, 632 (1937); *C. A.*, **31**, 5779 (1937); Norris and Ingraham, *THIS JOURNAL*, **60**, 1421 (1938).

(4) Kane and Lowy, *ibid.*, **58**, 2605 (1936).

(5) Kunkell and Ulex, *J. prakt. Chem.*, [2] **86**, 518 (1912).

(6) Sowa, Hennion and Nieuwland, *THIS JOURNAL*, **57**, 709 (1935).

(7) O'Connor and Sowa, *ibid.*, **60**, 125 (1938).