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} 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} 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} 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} 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} 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[1]

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,[2] methyl alcohol,[3] methyl sulfate[4] and methyl chlorocarbonate.[5] 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[6] 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.[7]

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) Kunckell 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).

<div align="center">TABLE I</div>

<div align="center">ALKYLATION OF PHENOL AND ANISOLE WITH METHYL ETHER–BORON FLUORIDE</div>

Compounds	Wt., g. (moles)	Me₂OBF₃ Wt., g. (moles)	Heating time, hrs.	Anisole g. (moles)	Mono, g.	Di, g.	Tri, g.	Tetra, g.	Penta, g. (moles)
Phenol	47 (0.5)	85.5 (0.75)	2	28 (0.26)	3				
Phenol	141 (1.5)	114 (1)	6	97.5 (0.90)	5.5				
Phenol	94 (1)	228 (2)	12	32 (0.30)	14	5	5	10	14 (0.08)
Phenol	70.5 (0.75)	285 (2.5)	14	29 (0.27)	10	7	1	3	12.5 (0.07)
Phenol	94 (1)	670 (5)	32	8 (0.07)	13	12	3	15	78 (0.44)
Anisole	54 (0.5)	171 (1.5)	14	24 (0.22)	4.5	4	2	4	10 (0.06)
Anisole	27 (0.25)	114 (1)	19	14 (0.13)	4	1	1	2	6 (0.03)

and anisole. The method is of practical interest for several reasons. Either methyl alcohol or by-product methyl ether from the methanol synthesis may be used as a starting material. The process can be applied directly to oxygenated aromatic compounds such as phenol and anisole.

Like the Friedel–Crafts reaction this method usually gives a mixture of products resulting from the introduction of one or more methyl groups in the several possible positions. In methylation by means of both aluminum chloride and boron fluoride, it appears possible to introduce a larger number of groups than is the case when larger alkyl groups are employed. For instance in the present work it was found possible to completely methylate phenol to pentamethylanisole. It was also found possible to polymethylate naphthalene, but the products could not be separated into definite compounds.

Experimental Part

Methyl Ether–Boron Fluoride.—Since methyl ether is not ordinarily available in laboratories, the preparation of methyl ether–boron fluoride from methyl alcohol was used.[8] A good procedure was as follows. Two hundred and twenty grams (approximately 3 moles) of boron fluoride was passed into 128 g. (4 moles) of methyl alcohol in a 1-liter 3-necked flask equipped with a reflux condenser and sealed stirrer. About three hours was required for the addition of the boron fluoride, the rate of addition being such that a slow rate of reflux was maintained.

A 95% yield of methyl ether–boron fluoride was obtained on distillation, b. p. 127–128°, d^{25}_4 1.2348.

Anisole and Methylated Anisoles.—Since the procedure was quite uniform for all of the reactions, only one general procedure is given.

The phenol or anisole and the methyl ether–boron fluoride were placed in a 1-liter 3-necked flask equipped with a reflux condenser and a sealed stirrer. The flask was heated to reflux temperatures for varying lengths of time. After the reaction mixture was cool, it was poured into an ice-cooled solution of concentrated sodium hydroxide and extracted with ether. The ether layer was washed five to eight times with a 25% solution of sodium hydroxide, then

(8) Gasselin, *Ann. chim.*, [7] **3**, 28 (1894).

water, dried over calcium chloride and carefully fractionated through a Widmer column. The distillation was stopped when the pentamethylanisole solidified in the condenser, the temperature at this point being 115° at 6 mm. The pentamethylanisole was steam distilled from the residue and crystallized from ether. Recrystallization from ether gave white plates, m. p. 119°. Table I gives the essential data concerning the separate experiments.

The alkaline solution, from the ether extractions, on acidification gave varying quantities of phenol and alkylated phenols which were not isolated as definite compounds.

Methylated Naphthalenes.—Thirty-one grams (0.25 mole) of naphthalene and 114 g. (1 mole) of methyl ether–boron fluoride were heated at reflux temperature for forty hours. Distillation of the reaction mixture, after treatment as above, gave 3 g. of naphthalene and small quantities of probable mono- and dimethylated compounds. The major portion of the reaction mixture boiled above 210° at 6 mm.

Identification of Pentamethylanisole.—Due to the fact that the pentamethylanisole steam distilled and solidified in the condenser, a slight modification of the ordinary Zeisel method was used for the determination of methoxyl percentage. Fifteen ml. of 50% hydriodic acid and 9 ml. of acetic anhydride were cooled and placed in a cooled glass tube and 0.2 to 0.3 g. of sample was added. The tube was sealed and heated for two hours at 135° in an oil-bath. The tube was allowed to cool, placed in a salt–ice bath for an hour, opened, attached as rapidly as possible to the Zeisel apparatus and the determination completed in the usual manner.

Treatment of pentamethylanisole with fuming nitric acid and concentrated sulfuric acid gave no nitrated products, the original compound being recovered after heating for two hours on a water-bath. The fraction boiling immediately below pentamethylanisole, suspected of containing tetramethylanisoles, nitrated very vigorously when treated in the same manner, to give a solid compound, m. p. 189°.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18; MeO, 17.41; mol. wt., 178.26. Found: C, 80.80; H, 10.23; MeO, 16.96; mol. wt. (cryoscopic in benzene), 174.5.

Pentamethylphenol.—Pentamethylphenol was obtained by cleaving pentamethylanisole with 50% hydriodic acid in the presence of acetic anhydride in a sealed tube at 135°. The contents of the tube were poured into 500 ml. of water and filtered. The solid was treated with hot 25% sodium hydroxide solution, cooled, filtered and the filtrate was acidified with concentrated sulfuric acid, a white, flocculent

precipitate being obtained. The precipitate was dissolved in acetone, filtered and the pentamethylphenol allowed to crystallize, m. p. 128°.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82; mol. wt., 164.24. Found: C, 79.62; H, 10.10; mol. wt. (cryoscopic in benzene), 161.9.

Summary

A new method for methylating aromatic compounds is reported, using methyl ether–boron fluoride as a methylating agent. The method has some advantages over methylation by means of the Friedel–Crafts reaction.

The complete methylation of phenol has been accomplished.

Further work is being done in this Laboratory on the use of methyl ether–boron fluoride as a methylating agent.

4,4-Dimethoxy-1,4-diphenyl-1,3-butanedione Enol

By Robert E. Lutz and James M. Smith, Jr.

1,4-Diphenyl-4,4-dimethoxy-1,3-butanedione enol (I), derived from 1,4-diphenyl-1,2,4-butanetrione enol (II) through methylation of the 1-keto group, was obtained purely by accident and has been investigated because of its close relationship both to β-diketones and to the 1,2,4-triketone enols which have been the subject of recent studies in this Laboratory.[1] It was obtained in 10–15% yields as a by-product in the benzoylation of diphenylbutanetrione sodium enolate (II). In this reaction the products usually isolated were the previously described[1] oxygen and carbon benzoyl derivatives VI and VII.[2] The ketal enol (I) was obtained regularly in addition to these products when the solvent, isopropyl ether, was partly evaporated and methanolic sodium hydroxide was then added slowly to the reaction mixture (the original object of this procedure was to hydrolyze the oxygen–benzoyl products directly and facilitate the isolation of the carbon–benzoyl product). The formation of the ketal grouping evidently resulted from rapid acid-catalytic methylation of the terminal carbonyl group of an intermediate oxygen–benzoyl product, probably IV, the necessary acid being produced through liberation of hydrogen chloride by

methanolysis of the excess benzoyl chloride before sufficient alkali had been added to complete the neutralization and hydrolysis. The ketal enol evidently is formed first as its benzoate (V) and is not actually liberated in the free enolic state (I) until after the digestion with excess alkali at the end of the procedure. The probable sequence of reactions is outlined in the first diagram and the proof of structure of the ketal enol and evidence supporting the proposed mechanism of its formation are treated in the following discussion.
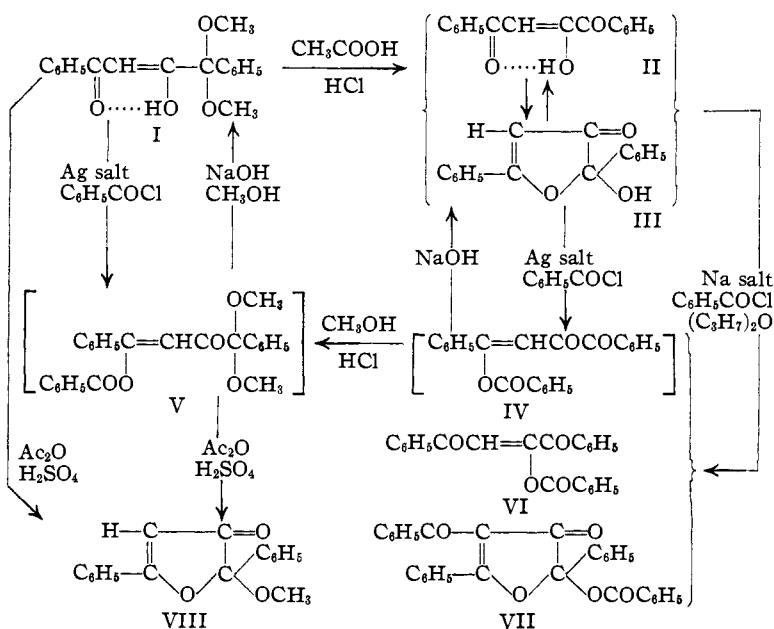
(1) Lutz and Stuart, This Journal, (a) **58**, 1885 (1936); **59**, (b) 2316, (c) 2322 (1937); Lutz and Wood, *ibid.*, **60**, (d) 229, (e) 705 (1938).

(2) Further details and discussion on these two products will be presented in later papers.

The ketal enol contains two methoxyl groups. It reacts with sodium carbonate or sodium hydroxide, and gives sodium and silver salts, both