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

Alkylation of Benzene with Alcohols, Boron Fluoride and Assistants[1]

BY N. F. TOUSSAINT AND G. F. HENNION

Introduction

The alkylation of benzene with monohydric alcohols has received relatively little attention. The reactions proceed only in the presence of strong dehydrating agents such as zinc chloride,[2] sulfuric acid,[3] aluminum chloride,[4] and boron fluoride.[5]

Disadvantages of the reported procedures are a frequent need for autoclave or sealed tube methods and/or excessive amounts of condensing agent; products are often impure and yields unsatisfactory. Furthermore, these methods have not been applied to the higher alcohols now available from the hydrogenolysis of fats.

Because long-chain alkylbenzenes have possible utility in the field of detergents and wetting agents the authors have reinvestigated alcohol–benzene reactions with boron fluoride.[5] It was desired particularly to apply the method to various primary alcohols and to improve yields of monoalkyl products. It was soon observed that boron fluoride is assisted remarkably in these reactions by various acidic dehydrating agents as phosphorus pentoxide, sulfuric acid and benzenesulfonic acid. The effect of these secondary condensing agents is particularly marked with the primary alcohols. Data for a number of experiments are given in Table I.

Alkylation apparently occurs without carbon skeleton rearrangement. However, only secondary and tertiary alkyl benzenes have been made in this manner. While the reaction mechanism is in doubt, the products are those which would be formed by dehydration of the alcohol to olefin and addition of benzene according to Markownikoff's rule. The dialkyl derivatives are the para compounds.[5] Methylation and ethylation were unsuccessful.

Physical properties for the compounds are given in Table II. Analyses for octyl- and dodecylbenzene are given in Table III.

Procedure

Reagents.—Boron fluoride was purchased from the Harshaw Chemical Co. *n*-Octyl and *n*-dodecyl alcohols were furnished by the du Pont Co. Other alcohols were from Eastman Kodak Co. Benzenesulfonic acid was prepared as previously described.[6]

***s*-Butylbenzene (Expt.** 10).—Two moles (156 g.) of benzene and 0.5 mole (37 g.) of *n*-butyl alcohol were placed in a one-liter three-necked flask equipped with a reflux condenser and motor-driven mercury-sealed stirrer. The solution was cooled in a bath of cold water and boron fluoride admitted, with stirring, until 0.5 mole (34 g.) had been absorbed. Then 0.125 mole (17.7 g.) of phosphorus pentoxide was added quickly. The mixture was warmed *slowly*, with stirring, to reflux temperature and soon became homogeneous. On continued heating the solution became turbid and stratified into two layers when agitation was discontinued. Further heating caused gradual diminution in the volume of the lower layer. After heating for three hours the layers were separated and the upper one washed, neutralized, dried and fractionally distilled. There was obtained 50 g. (74.5%) of *s*-butylbenzene and 3 g. (6.3%) of *p*-di-*s*-butylbenzene.

***s*-Amylbenzene (Expt. 32).**—Sulfuric acid (25 g., 94% acid) was added to a solution of *n*-amyl alcohol (44 g., 0.5 mole) in benzene (312 g., 4.0 moles) previously saturated with boron fluoride (34 g., 0.50 mole). After heating for five and one-half hours the upper layer was separated and treated as above. Distillation gave 59.2 g. (80%) of *s*-amylbenzene.

Miscellaneous.—All experiments with phosphorus pentoxide gave homogeneous solutions after brief heating. Upon further reaction these separated into two layers, except in cases where dodecyl alcohol was used. Dodecylbenzene was distilled, *in vacuo*, from the crude reaction mixture, then washed, dried and redistilled.

In the sulfuric acid experiments with *n*-butyl alcohol (Expts. 25–29) three layers appeared after heating. The lowest layer was removed in each case and water added to the remaining layers. The hydrocarbon was then removed and treated in the conventional manner.

A condition of temporary homogeneity was observed only in experiments with phosphorus pentoxide. With sulfuric acid and benzenesulfonic acid separate phases persisted throughout the reaction periods.

Frequently dodecylbenzene gave troublesome emulsions when first washed with water. The emulsions were broken by addition of ether.

In the experiments with benzenesulfonic acid it was

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(1) Paper XXIII on organic reactions with boron fluoride; previous paper, THIS JOURNAL, **61**, 1463 (1939).

(2) Goldschmidt, *Ber.*, **15**, 1066, 1425 (1882).

(3) Brochet and Le Boulenger, *Compt. rend.*, **117**, 235 (1898); Verley, *Bull. soc. chim.*, [3] **19**, 67 (1898); Boedker, *ibid.*, [3] **31**, 966 (1904); Meyer and Bernhauer, *Monatsh.*, **53**, 721 (1929); Kirrmann, *Bull. soc. chim.*, [4] **51**, 451 (1932); Kirrmann and Graves, *ibid.*, [5] **1**, 1494 (1934).

(4) Huston, *et al.*, THIS JOURNAL, **38**, 2531 (1916); **40**, 785 (1918); **48**, 1955 (1926); **56**, 2432 (1934); Tzukervanik, *J. Gen. Chem.* (*U. S. S. R.*), **5**, 117, 764 (1935); **31**, 5779 (1937); Norris and Ingraham, THIS JOURNAL, **60**, 1421 (1938).

(5) Sowa and McKenna, *ibid.*, **59**, 470 (1937).

(6) Thomas, Anzilotti and Hennion, *Ind. Eng. Chem.*, **32**, 408 (1940).

TABLE I

ALKYLATION OF BENZENE WITH ALCOHOLS IN THE PRESENCE OF BORON FLUORIDE

Expt.	Moles ROH	Moles C_6H_6	Moles BF_3	Moles Asst. reagent	Time, hr.	Yield, % Mono	Yield, % Di
			A. Assisted by Phosphorus Pentoxide				
1	0.5 *n*-C_3	2.0	0.5	0	5	5.4	0
2	.5 *n*-C_3	2.0	.5	.12	3	58.5	13
3	.5 *i*-C_3	2.0	.5		3	40.0	19.8
4	.5 *i*-C_3	2.0	.5	.12	3	37.5	19.8
5	.5 *n*-C_4	1.0	.5		4	0	0
6	.5 *n*-C_4	2.0	.4	.12	3	37.4	6.3
7	.5 *n*-C_4	2.0	.33	.17	3	55.3	10.5
8	.5 *n*-C_4	2.0	.5	.12	3	73.2	8.3
9	.5 *n*-C_4	1.0	.5	.12	2.5	73.2	14.7
10	.5 *n*-C_4	2.0	.5	.12	3	74.5	6.3
11	.5 *s*-C_4	2.0	.5		3	51.5	11.8
12	.5 *s*-C_4	2.0	.5	.12	3	46.2	12.7
13	.5 *i*-C_4	2.0	.5		3	47.8	14.7
14	.5 *i*-C_4	2.0	.5	.12	3	56.7	11.8
15	.5 *t*-C_4	2.0	.25		3	28.4[a]	..
16	.5 *t*-C_4	2.0	.25	.12	3	24.6[a]	..
17	.25 *n*-C_5	2.0	.25		5.5	0	0
18	.25 *n*-C_5	2.0		.07	5.5	0	0
19	1.0 *n*-C_5	1.0	1.0	.25	1	19.6	10.5
20	0.5 *n*-C_5	0.5	0.5		2	32.2	26.8
21	2.0 *n*-C_5	4.0	2.0	.5	2	66.4	14.2
22	0.5 *n*-C_5	4.0	0.5	.12	6	85.0	0
23	1.0 *n*-C_8	8.0	1.0	.25	3	79.0	0
24	0.5 *n*-C_{12}	4.0	0.5	.25	16	33.3	0
			B. Assisted by Sulfuric Acid				
25	0.5 *n*-C_4	1.0	0.5	0.5	4	12.7	11.0
26	.5 *n*-C_4	2.0	.75[b]	1.0	4	22.4	4.2
27	.5 *n*-C_4	2.0	.5	1.5	4	19.5	0
28	.5 *n*-C_4	2.0	.5	0.5[c]	3	37.4	0
29	.5 *n*-C_4	2.0	.5	1.0[c]	3	7.5	0
30	1.0 *n*-C_5	1.0	.5	0.5	2	30.2	9.1
31	0.5 *n*-C_5	4.0		.75	5.5	20.2[d]	0
32	.5 *n*-C_5	4.0	.5	.25	5.5	80.0	0
33	.5 *n*-C_{12}	2.0	.5	1.0	10	46.4	0
			C. Assisted by Benzenesulfonic Acid				
34	0.5 *n*-C_4	2.0	0	0.5	4	0	0
35	1.0 *n*-C_4	4.0	1.5[e]	1.0	4	68.5	0
36	0.5 *n*-C_4	2.0	0.5	0.5	4	63.0	0
37	.5 *n*-C_5	2.0	.5	.5[f]	5.5	19.5	7.3
38	.5 *n*-C_{12}	2.0	.5	.5	10	44.6	0

[a] Contains polymer, presumably triisobutylene. [b] Added H_2SO_4 before BF_3. [c] 100% H_2SO_4, others were 94% H_2SO_4. [d] After first distillation. [e] Includes $BF_3 \cdot H_2O$ from preparation of benzenesulfonic acid. [f] Recovered from Exp. no. 35.

TABLE II

PHYSICAL CONSTANTS OF PRODUCTS

Expt.	Alkylbenzene	Boiling point, °C.	Mm.	d^{20}	$n^{20}D$
2	*i*-C_3	151–2	744	0.8619	1.4912
10	*s*-C_4	170–2	744	.8624	1.4900
13	*t*-C_4	165–9	746	.8660	1.4918
22	*s*-C_5	189–90	744	.8621	1.4890
23	*s*-C_8	123–5	20	.854	1.4837
24	*s*-C_{12}	182–4	20	.855	1.4818
2	*p*-di-*i*-C_3	200–8	744	.860	1.490
8	*p*-di-*s*-C_4	236–8	744	.862	1.489
13	*p*-di-*t*-C_4	234–6	746	m. p., 77°	
21	*p*-di-*s*-C_5	141–6	20	.863	1.495

TABLE III

ANALYSES

Expt.	Alkylbenzene	%, C Calcd.	%, C Found	% H Calcd.	% H Found	Mol. wt. Calcd.	Mol. wt. Found
23	*i*-C_8H_{17}	88.4	88.6	11.6	11.0	190	182
24	*i*-$C_{12}H_{25}$	87.6	88.0	12.3	12.2	246	243

found possible to recover boron fluoride, as the dihydrate, from the acid layers by addition of the calculated amount of water and distillation.[6] Boron fluoride was thus recovered as $BF_3{\cdot}2H_2O$, b. p. 91° at 25 mm., from Expt. 35 in 95% yield.

Further work is in progress.

Summary

1. Certain acidic dehydrating agents assist boron fluoride as a condensing agent in the alkylation of benzene with primary alcohols.

2. Data are given for thirty-eight experiments, showing the influence of conditions upon yields of products.

3. Normal and secondary alcohols give secondary alkylbenzenes. Iso and tertiary butyl alcohol gave *t*-butylbenzene. Dialkylation proceeds mainly para.

4. Alcohols as high as dodecyl have been used successfully.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Chlorination and the Structure of Acetylketene

BY CHARLES D. HURD AND J. L. ABERNETHY

The recent paper[1] by Boese on "diketene" mentions that this substance "rapidly absorbs chlorine at low temperatures to yield γ-chloroacetoacetyl chloride" and states that it is "stable only at low temperatures and cannot be purified by distillation." Since no details were listed, this note is submitted in view of our similar work on the same compound.

Chlorine was passed into an ice-cold, vigorously-stirred solution of 7 cc. of acetylketene in 20 cc. of carbon tetrachloride until there was a 6-g. increase in weight. The mixture was slightly yellow in color. Distillation of the solvent with a steam-bath left an orange-colored residue of chloroacetoacetyl chloride, $ClCH_2COCH_2COCl$, which was vacuum distilled. Extensive decomposition occurred, but 1.5 cc. of the acid chloride was obtained at 93–96° (8 mm.), or 117–119° (17 mm.). The distillate was orange colored and fumed in moist air. A black tar remained in the distilling flask. These physical constants were obtained for the chloroacetoacetyl chloride: $d^{20}{}_4$ 1.4397; $n^{20}{}_D$ 1.4860; mol. rotation, calcd. 30.77, found 30.89.

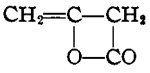
Anal. Calcd. for $C_4H_4O_2Cl_2$: Cl, 45.7. Found: Cl, 45.2, 45.1.

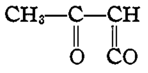
Chloroacetoacetyl chloride was converted to ethyl chloroacetoacetate, $ClCH_2COCH_2COOC_2H_5$, as follows. Five cc. of acetylketene in 30 cc. of carbon tetrachloride was treated with chlorine until 4.5 g. had been absorbed. Then, without distillation, the solution was poured slowly into an excess of absolute alcohol at 0°. On distillation, 6 cc. of the ethyl ester was collected at 117–119° (17 mm.). This ester has been made in other ways by several investigators.[2]

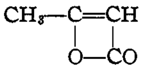
Chloroacetoacetanilide, $ClCH_2COCH_2CONHC_6H_5$, was obtained by mixing pure chloroacetoacetyl chloride with an equivalent amount of aniline in benzene. The aniline hydrochloride was removed by washing with water. Then the benzene was distilled off and the resulting anilide was crystallized from ether. The melting point was 140–141°.

Anal. Calcd. for $C_{10}H_{10}O_2NCl$: N, 6.61. Found: N, 6.75, 6.71.

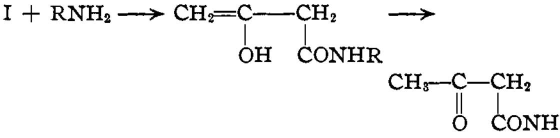
Boese adopts vinylaceto-β-lactone (I) as a preferred structure for ketene dimer. With


I


$$\mathrm{CH_3{-}\underset{\substack{\|\\ O}}{C}{-}\underset{\substack{\|\\ CO}}{CH}}$$
II


III

(I) addition reactions with alcohols or amines may be explained by assuming reaction at the lactone position, followed by tautomerization


$$\mathrm{I} + \mathrm{RNH_2} \longrightarrow \mathrm{CH_2{=}\underset{\substack{\mid\\ OH}}{C}{-}\underset{\substack{\mid\\ CONHR}}{CH_2}} \longrightarrow \mathrm{CH_3{-}\underset{\substack{\|\\ O}}{C}{-}\underset{\substack{\mid\\ CONHR}}{CH_2}}$$

Hydrogenation to butyro-β-lactone must involve addition at the double bond. Neither of these reactions are critical for purposes of structure

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[1] Boese, *Ind. Eng. Chem.*, **32**, 20 (1940).

[2] Lespieau, *Compt. rend.*, **138**, 422 (1904); Picha, Doht and Weisl, *Monatsh.*, **27**, 1247 (1906); Schlotterbeck, *Ber.*, **42**, 2570 (1909); Alexandrow, *ibid.*, **46**, 1022 (1913).