perature of the bath. The vapors then passed into the reaction tube "B." This tube was constructed from 2 meters of 18-mm. Pyrex tubing wound into one continuous coil. It contained about 5 g. of zirconium oxide supported on granulated pumice. With such a small amount of catalyst the adsorption effects were found to be relatively small. The original catalyst was used throughout the investigation. The vapors leaving the reaction coil passed into the condenser where they were condensed and carried back into the bulb "A." The side arm at "D" was closed by means of a piece of rubber tubing plugged with glass rod. By applying suction to this tube the apparatus could be emptied of liquid and vapor at the end of a run.

At the beginning of a run as soon as the vapors reached the condenser the rubber tubing on the end of the male part of the ground glass joint was closed and the reaction mixture was refluxed over the catalyst for several days. After a reasonable time had been allowed for equilibrium to be reached the stopcock was closed and the tube leading from the reaction coil to the condenser was heated with a free flame in order to drive over any liquid which might have condensed there after the stopcock was closed. A 10-ml. sample was then pipetted into a 25-ml. weighing flask and weighed. The contents of the weighing flask were carefully washed into a titrating flask and titrated with 0.5 *N* sodium hydroxide. Refluxing was begun again and continued for from one to five days and another sample was removed. Constancy of the acid content was taken to indicate that equilibrium had been reached.

The time allowed for a run depended upon the temperature and varied from nine to eleven days at 200° to from three to four weeks at 125°. For the esterification reaction at the lower temperatures the reaction mixture was refluxed over the catalyst for four or five days at 200° and then the temperature was dropped to 150 or 125° and refluxing continued for from two to three weeks. For hydrolysis at the lower temperatures the same procedure was followed except that the refluxing at 200° was permitted to continue until the two layers had almost disappeared.

The authors wish to express their thanks to Mr. I. J. Terry for his assistance and interest during the progress of this work.

Summary

The equilibrium of the vapor phase esterification of ethyl alcohol by acetic acid over zirconium oxide has been studied by a static method at 200, 150 and 125°. From the data obtained the equilibrium constants and standard free energies for this reaction at these temperatures have been calculated.

TALLADEGA, ALABAMA RECEIVED AUGUST 13, 1942

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

Some Friedel–Crafts Type Alkylations with Boron Trifluoride[1]

BY G. F. HENNION AND R. A. KURTZ

Introduction

While boron trifluoride is now well recognized as a catalyst for the alkylation of aromatic compounds with alcohols,[2] olefins,[3] esters,[4] and ethers,[5] this method has not been applied successfully to similar reactions with the organic halides. Thus boron trifluoride has not served as a substitute for aluminum chloride in Friedel–Crafts alkylations with alkyl halides. Solutions of alkyl halide in anhydrous benzene, for example, do not dissolve boron trifluoride, nor is there evidence of reaction. It has now been found that if a moderate quantity of water, alcohol or other polar compound reactive to boron trifluoride is used also, many active halides alkylate rapidly and in fair yield as shown in Table I.

With benzene and toluene tertiary chlorides and benzyl chloride gave the best yields. Secondary halides gave low yields, which, however, could be increased markedly by the use of sulfuric acid along with water and boron trifluoride. The normal chlorides and bromides were found to be almost wholly unreactive.

An interesting feature of this general method lies in the fact that the lower layers which separate when the reactions are complete may be reused without loss of activity, particularly if resaturated with boron trifluoride to make up for volatilization losses.

Along with the halide one may use the corresponding alcohol, water, methanol or even acetic acid. It therefore cannot be argued that hydrolysis of the halide to the corresponding alcohol with subsequent alkylation by the latter, is necessarily involved in these reactions. The positive fragment mechanism serves well to explain our

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[1] Paper XXVI on organic reactions with boron trifluoride; previous paper, THIS JOURNAL, **63**, 2603 (1941).

[2] McKenna and Sowa, *ibid.*, **59**, 470 (1937); Toussaint and Hennion, *ibid.*, **62**, 1145 (1940); Welch and Hennion, *ibid.*, **63**, 2603 (1941).

[3] Slanina and Sowa, *ibid.*, **57**, 1547 (1935); Wunderly, Sowa and Nieuwland, *ibid.*, **58**, 1007 (1936); Ipatieff and Grosse, *ibid.*, **58**, 2339 (1936).

[4] McKenna and Sowa, *ibid.*, **59**, 1204 (1937).

[5] O'Connor and Sowa, *ibid.*, **60**, 125 (1938); Monacelli and Hennion, *ibid.*, **63**, 1722 (1941).

TABLE I

THE ALKYLATION OF BENZENE AND TOLUENE WITH ALKYL HALIDES

Reagents (moles) Halide	Hydrocarbon	Catalyst	Heating time, hr.	Alkylation, % Mono	Di
t-C_4Cl(0.8)	C_6H_6(2)	*t*-C_4OH(0.2) + BF_3(0.13)	5	46	10
t-C_4Cl(1)	C_6H_6(2)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.2)	2.5	46	16
t-C_5Cl(0.8)	C_6H_6(2)	*t*-C_5OH(0.2) + BF_3(0.13)	5.5	43	Trace
t-C_5Cl(1)	C_6H_6(2)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.17)	5.5	53	Trace
$PhCH_2Cl$(0.8)	C_6H_6(2)	$PhCH_2OH$(0.2) + BF_3(0.15)	13	12	4
$PhCH_2Cl$(1)	C_6H_6(2)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.2)	7.5	59	2
i-C_3Br(0.5)	$C_6H_5CH_3$(1)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.2)	9	18	
i-C_3Br(0.5)	$C_6H_5CH_3$(1)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.2) + 23 g. H_2SO_4	8	50	
s-C_4Cl(0.5)	$C_6H_5CH_3$(1)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.2)	6.5	22	
s-C_4Cl(0.5)	$C_6H_5CH_3$(1)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.2) + 48 g. H_2SO_4	6.5	40	
t-C_4Cl(0.5)	$C_6H_5CH_3$(1)	$BF_3 \cdot 2H_2O$(0.2)	3.5	40	
t-C_4Cl(0.8)	$C_6H_5CH_3$(2)	*t*-C_4OH(0.2) + BF_3(0.15)	5	68	
t-C_4Cl(1)	$C_6H_5CH_3$(2)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.2)	2	66	
t-C_4Cl(1)	$C_6H_5CH_3$(2)	C_4OH(0.29) + BF_3(0.29)	3	64	
t-C_4Cl(1)	$C_6H_5CH_3$(2)	CH_3COOH(0.2) + BF_3(0.15)	6	65	
t-C_5Cl(0.8)	$C_6H_5CH_3$(2)	*t*-C_5OH(0.2) + BF_3(0.14)	6	52	
t-C_5Cl(1)	$C_6H_5CH_3$(2)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.13)	5	66	
3-Br-C_5(0.5)	$C_6H_5CH_3$(1)	3-OH-C_5(0.15) + BF_3(0.14)	5.5	12	
3-Br-C_5(0.5)	$C_6H_5CH_3$(1)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.19)	5	17	
3-Br-C_5(0.5)	$C_6H_5CH_3$(1)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.11) + 20 g. H_2SO_4	10	58	
$PhCH_2Cl$(1)	$C_6H_5CH_3$(2)	$BF_3 \cdot 2H_2O$(0.2) + BF_3(0.15)	5	70	5
Allyl Cl(1)	$C_6H_5CH_3$(2)	$BF_3 \cdot 2H_2O$(0.58) + BF_3(0.58)	8	14[a]	

[a] Obtained 0.14 mole of 1,2-di-*p*-tolylpropane.

results as shown by the following equations.

$$R—Cl + H_2O \rightarrow BF_3 \longrightarrow R^+ + (HOBF_3)^- + HCl$$

$$R^+ + ArH \longrightarrow ArR + H^+$$

The dialkylated benzenes and alkyl toluenes were found to have the para structures as shown by oxidation to terephthalic acid, identified as the dimethyl ester. Physical constants are listed in Table II and some analyses in Table III.

TABLE II

PHYSICAL CONSTANTS OF PRODUCTS

Compound	B. p. °C.	Mm.	n^{20}_D	d^{20}_4	M. p., °C.
t-Butylbenzene	165–166	735	1.4919	0.8665	
t-Amylbenzene	191–192	735	1.4920	.8660	
Diphenylmethane	90–91	4	1.5770		25–25.5
p-Isopropyltoluene	173–174	735	1.4956	.8678	
p-*s*-Butyltoluene	80	19	1.4938	.8665	
p-*t*-Butyltoluene	186–187	735	1.4919	.8628	
p-*t*-Amyltoluene	86	12	1.4952	.8711	
3-*p*-Tolylpentane	85	13	1.4940	.8694	
p-Benzyltoluene	114–115	3	1.5712	.9976	
1,2-Di-*p*-tolylpropane	142–144	5	1.5565	.9726	
Dibenzyltoluene	214–217	4	1.5991	1.0413	
p-Di-*t*-butylbenzene					76.5–77
p-Dibenzylbenzene					80–81
Dimethyl terephthalate					139–140

TABLE III

ANALYSES OF SOME REACTION PRODUCTS

Compound	Mol. wt. Calcd.	Obsd.	% Carbon Calcd.	Obsd.	% Hydrogen Calcd.	Obsd.
p-*t*-Amyltoluene	162	162	88.9	89.0	11.1	11.0
3-*p*-Tolylpentane	162	162	88.9	88.7	11.1	11.3
1,2-Di-*p*-tolylpropane	224	220	91.1	90.5	8.9	9.5

Experimental

The boron trifluoride dihydrate was prepared according to the method of Meerwein and Pannwitz.[6]

The reactor consisted of a one-liter, three-necked round-bottom flask in which was placed the aromatic compound, the acetic acid, alcohol or the boron trifluoride dihydrate, and the alkyl halide. The flask was then placed in a cold water-bath and boron trifluoride introduced beneath the surface of the liquid. (When concentrated sulfuric acid was used as an added catalyst it was added at this point and the contents resaturated with boron trifluoride. In the reaction with allyl chloride and toluene the procedure was changed somewhat. Instead of adding the halide at once, it was diluted with toluene and the solution added dropwise from a separatory funnel into a stirred and heated toluene catalyst mixture.) After fitting the flask with a mercury seal stirrer, reflux condenser, and thermometer extending below the level of the liquid, the flask and its contents were heated to the reflux temperature. The liquid was held at the reflux temperature, which gradually increased, throughout the heating period. On completion of the reaction the contents of the flask was transferred to a separatory funnel and the lower layer drawn off. The hydrocarbon layer was washed with saturated sodium chloride solution, saturated sodium carbonate solution,

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(6) Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 124 (1934).

again with saturated brine, dried over calcium chloride, and distilled through an efficient column.

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Summary

1. The alkylation of benzene and toluene with secondary, tertiary and allyl type halides has been accomplished with boron trifluoride catalysts.

2. The presence of water, alcohol or other polar compound reactive to boron trifluoride is necessary for reaction at atmospheric pressure.

3. Lower layers which separate from these reactions have been resaturated with boron trifluoride and reused without loss of catalytic activity.

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Preparation of Allyl and Methallyl Methacrylates by the Thermal Decomposition of Allyl and Methallyl α-Acetoxyisobutyrates

BY CHESSIE E. REHBERG, C. H. FISHER AND LEE T. SMITH

Considerable information concerning the thermal decomposition of α-hydroxypropionic acid and its derivatives has been collected in connection with an investigation of the pyrogenic conversion of lactic acid derivatives[1,2,3] into acrylic esters. It has been shown[4] that pyrolysis of methyl and benzyl α-acetoxypropionates (I, R = H or C_6H_5) gives high yields of methyl and benzyl acrylates, respectively. On pyrolysis ethyl and butyl α-acetoxypropionates (II, R = H or C_2H_5), which have hydrogen atoms on the beta-carbon atom of the alcohol group, yield olefins as well as acrylic esters. As a result of this undesirable side reaction (shown in equation II), the satisfactory preparation of acrylic esters by thermal decomposition of alkyl α-acetoxypropionates seems limited to derivatives, such as the methyl and benzyl esters (I), which lack hydrogen atoms on the beta-carbon atom.[5,6]

$$\text{(I)}\quad CH_3COOCH(CH_3)COOCH_2R \longrightarrow$$
$$\text{(R = H or } C_6H_5\text{)}\qquad CH_2{=}CHCOOCH_2R + CH_3COOH$$

$$\text{(II)}\quad CH_3COOCH(CH_3)COO\underset{\alpha}{CH_2}\underset{\beta}{CH_2}R \longrightarrow$$
$$\text{(R = H or } C_2H_5\text{)}$$
$$CH_2{=}CHR + CH_3COOCH(CH_3)COOH \longrightarrow CH_3COOH + CH_3CHO + CO$$

In a recent report[2] it was disclosed that allyl and methallyl α-acetoxypropionates, which have one hydrogen atom or none on the beta carbon atom of the alcohol group, on pyrolysis decompose into allyl and methallyl acrylates, respectively. In spite of the absence or paucity of beta hydrogen atoms, however, the desired acrylic esters were obtained only in 40% yields. The purpose of the present work was to compare the behavior of allyl and methallyl α-acetoxyisobutyrates (III) on pyrolysis with that of the corresponding α-acetoxypropionic acid derivatives and to develop satisfactory pyrogenic methods of producing allyl and methallyl methacrylates.

$$\text{(III)}\quad CH_3COOC(CH_3)_2COOCH_2CR{=}CH_2 \longrightarrow$$
$$\text{(R = H or } CH_3\text{)}\qquad CH_3COOH + CH_2{=}C(CH_3)COOCH_2CR{=}CH_2$$

It might be predicted from previous investigations[4,7,8] that derivatives of α-hydroxyisobutyric acid, which may be regarded as a tertiary alcohol, would decompose into methacrylic esters more readily than lactic acid derivatives would decompose into acrylic esters. Comparable data reported by Burns, Jones and Ritchie[4,7] on the thermal decomposition of derivatives of lactic and α-hydroxyisobutyric acids are given in Table I. These data indicate that derivatives of α-hydroxyisobutyric acid are more suitable than lactic acid derivatives for pyrogenic conversion into unsaturated products. Milder conditions sufficed for the pyrolysis, and in most instances better yields were obtained. Burns, Jones and

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(1) Smith, Fisher, Ratchford and Fein, *Ind. Eng. Chem.*, **34**, 473 (1942).

(2) Fisher, Rehberg and Smith, THIS JOURNAL, **65**, 763 (1943).

(3) Smith, Fisher, Filachione, Ratchford and Fein, "Pyrolysis of Lactic Acid Derivatives. Methyl Lactate, Acetoxypropionic Acid, Acetoxypropionyl Chloride, and Alkyl Acetoxypropionates," presented before the Division of Organic Chemistry at the 103rd meeting of the American Chemical Society, Memphis, Tenn., April 20–24, 1942.

(4) Burns, Jones and Ritchie, *J. Chem. Soc.*, 400 (1935).

(5) Bilger and Hibbert, THIS JOURNAL, **58**, 823–825 (1936).

(6) Hurd and Blunck, *ibid.*, **60**, 2419–2425 (1938).

(7) Burns, Jones and Ritchie, *J. Chem. Soc.*, 714 (1935).

(8) Ritchie, *ibid.*, 1054 (1935).