[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride.[1] XIX. Condensation of Cyclopropane and Olefins with Acids

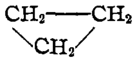
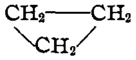
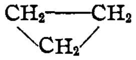
BY THOMAS B. DORRIS AND FRANK J. SOWA

In an earlier paper[2] a study was made of the condensation of propylene with acetic, benzoic and chloroacetic acids in the presence of boron fluoride.

The purpose of this investigation was to extend the olefin–acid condensation in order to determine the effect of various olefins and acids. Just as benzoic acid was found to undergo esterification without any nuclear substitution, so *p*-nitrobenzoic, *o*-chlorobenzoic, phenylacetic and furoic acids also underwent esterification when exposed to olefins and boron fluoride. *o*- and *p*-aminobenzoic acids did not react. Propylene, butylenes and amylenes yielded *s*- or *t*-alkyl esters, together with an abundance of polymeric products. Cyclopropane yielded the *n*-propyl esters.

TABLE I

ACIDS, UNSATURATED HYDROCARBONS AND BORON FLUORIDE

Acid	Mole	Solvent	BF_3, mole	Olefin	Time, hrs.	Ester	Yield, %
p-Nitrobenzoic	0.125	$C_2H_2Cl_4$	0.125	C_3H_6	1	*i*-Propyl[a]	14.5
o-Chlorobenzoic	.1	*i*-PrAc	.3	C_3H_6	72	*i*-Propyl[b]	45
o-Chlorobenzoic	.33	$C_2H_2Cl_4$	.2	C_3H_6[c]	2	*i*-Propyl	low[d]
o-or *p*-Aminobenzoic		$C_2H_2Cl_4$ or *i*-PrAc		C_3H_6		none[d]	
Phenylacetic	.25	$C_2H_2Cl_4$	.24	C_3H_6	56	*i*-Propyl[e]	40[d]
Furoic	.23	$C_2H_2Cl_4$	.32	C_3H_6	55	none[d]	
Acetic	1.41		.22	C_4H_8[f]		*t*-Butyl *s*-Butyl	32 8
Acetic	1.0		.62		25	*n*-Propyl[g]	65
Dichloroacetic	0.5		.125		8	*n*-Propyl[h]	59
Benzoic	0.125	$C_2H_2Cl_4$	.10		15	*n*-Propyl[i]	47

[a] M. p. 106–108°. [b] B. p. 118° (12 mm.), n^{25}_D 1.5085, d^{25}_4 1.1289. [c] Exothermic, with a temperature increase to 85°. [d] Extensive polymerization, with the product boiling over a wide range. [e] B. p. 157–165° (12 mm.), n^{25}_D 1.4845, d^{25}_4 0.9236. [f] A mixture of amylenes reacted similarly, but gave lower yields of esters. [g] B. p. 100°, n^{25}_D 1.3811, d^{25}_4 0.8625. [h] B. p. 167–170°, n^{25}_D 1.4360, d^{25}_4 1.2006. [i] B. p. 219–223°, n^{25}_D 1.4959, d^{25}_4 0.9958.

Experimental Part

Procedure.—The apparatus consisted of a three-necked round-bottomed flask containing an inlet and outlet tube and connected with a sealed-in stirrer.[3] The outlet was connected to a mercury sealed pressure regulator. Ordinarily, an equivalent amount of boron fluoride was added to a suspension of the acid in a solvent. The unsaturated hydrocarbon [propylene, a mixture of butylenes (80% iso, 20% alpha- and beta-), or cyclopropane] was passed in under a pressure of 90 cm. Together with the esters, there was much polymerized material from the experiments with propylene and butylenes. Essential data are collected in Table I.

The question of appropriate solvents for the aromatic acids used required much study. Most of the common oxygenated solvents are impractical, probably because coördination takes place between the oxygen atom of the solvent and the boron fluoride producing, as in the case of diethyl ether, a compound so stable that the boron fluoride exerts practically no catalytic effect unless a great excess is used. Of the liquids tried, tetrachloroethane served the best. Its toxicity, however, is a disadvantage and it seemed to promote polymerization of the olefin.

Cyclopropane with Sulfuric Acid.—The apparatus was the same as that previously employed.[3] Concentrated sulfuric acid (200 g.) was put in the three-necked flask and cooled to −3° while cyclopropane was added with vigorous stirring. When 160 g. of cyclopropane was absorbed the contents were poured carefully onto cracked ice, separated and again washed with cold water, dried over anhydrous sodium sulfate and distilled. A yield of 95% of di-*n*-propyl sulfate, b. p. 120° (20 mm.), was obtained. Propylene reacted according to the same procedure to give the theoretical yield of isopropyl sulfate, b. p. 98° (2 mm.).

Summary

A means of condensing olefins with acids, in the presence of boron fluoride, to form esters under mild conditions of temperature and pressure has been shown.

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(1) For previous paper, see O'Connor and Sowa, THIS JOURNAL, **60**, 125 (1938).

(2) Dorris, Sowa and Nieuwland, *ibid.*, **56**, 2689 (1934).

(3) Wunderly, Sowa and Nieuwland, *ibid.*, **58**, 1007 (1936).

It has been demonstrated that no nuclear condensation accompanied the formation of esters of benzoic, *o*-chlorobenzoic, *p*-nitrobenzoic and phenylacetic acids.

A method for the preparation of normal esters by the condensation of cyclopropane with acids has been described.

The preparation of normal and isopropyl sulfate has been described.

NOTRE DAME, INDIANA RECEIVED NOVEMBER 10, 1937

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA*]

The Transition of the Mercuric Sulfides in Anhydrous Hydrogen Sulfide in Ammonia[1]

BY G. B. HEISIG

No information is available to show the behavior of the black and red modifications of mercuric sulfide when suspended in anhydrous ammonia, hydrogen sulfide or mixtures of the two. The transition point is 386 ± 2° and the change from the black to the red form is exothermal (382 cal.). Quam[2] found that the red modification is formed on suspending mercuric chloride in liquid hydrogen sulfide. The formation of the stable red modification is not in agreement with Ostwald's rule[3] although the change may be so rapid that the formation of the black modification has not been recorded.

By analogy to the behavior of water, liquid ammonia should not catalyze the transition of the modifications but a solution of ammonium sulfide in liquid ammonia should hasten the change from the red to the black form. This would be expected from a statement by Franklin[4] that a black precipitate is formed on adding ammonium sulfide (in liquid ammonia) to a mercury salt, and that the composition is doubtless that of the familiar sulfide of mercury.

Apparatus.—The all glass apparatus in which experiments were conducted is shown in Fig. 1. The ammonia was obtained from commercial tanks. The hydrogen sulfide was obtained from tanks or prepared by the action by dilute sulfuric acid on ferrous sulfide. The gases were dried by passing through drierite (G and H). Some reaction occurred between the drying agent and ammonia. In some runs the ammonia was dried by passing over ribbon sodium. The amount of liquid ammonia and liquid hydrogen sulfide was measured in the graduated tubes E and F at the temperature of dry ice. The volume of the portion of the system between the stopcocks A and B as well as the cross section of the manometer tubes was known, making it possible to add known quantities of these substances in the gaseous state. There was practically no non-condensable gas in the tank ammonia or hydrogen sulfide. The measured gases were condensed in tubes like C, containing the samples of mercuric sulfide at the temperature of liquid oxygen. Non-condensable gases were removed with an oil pump protected by the trap I immersed in liquid air and the tubes were sealed off. Before opening, the tubes containing the samples were cooled in liquid oxygen. After being opened, some were sealed to a high vacuum system maintained at 10^{-5} mm. and the volatile material condensed in a liquid air trap. The contents of other tubes were brought onto filter paper in a vacuum jacketed funnel and washed thoroughly with liquid ammonia.

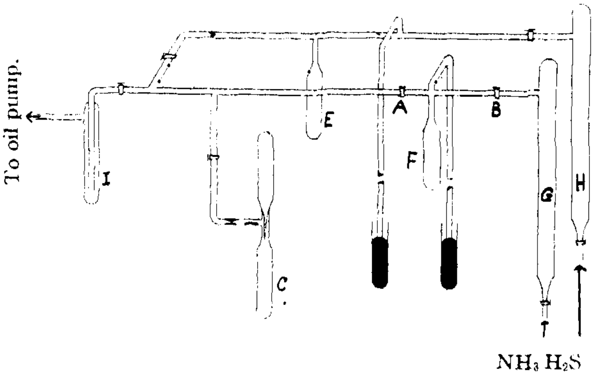

Fig. 1.

Materials.—The samples of black mercuric sulfide were commercial products containing 92.8% of mercuric sulfide (P_B) and 92.1% (M_B). Also samples were prepared by saturating a 0.3 *N* hydrochloric acid solution of mercuric chloride with hydrogen sulfide (z) and by heating a solution of mercuric chloride to which had been added sodium thiosulfate (w). These samples contained 99.5% of mercuric sulfide. The samples of the red modification were a commercial product (M_A and P_R) containing 99.6 and 98.7% of the sulfide, respectively.

Analysis.—The samples of the mercuric sulfide were dried for an hour at 106° and analyzed according to a modification of the method described by Rupp and Muller.[5]

(*) This work was started at the University of Illinois during the summer of 1935.

(1) Original manuscript received March 22, 1937.

(2) Quam, THIS JOURNAL, **47**, 105 (1925).

(3) Ostwald, "Fundamental Principles of Chemistry," Longmans, Green & Co., New York, N. Y., 1917, p. 92.

(4) Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corp., New York, N. Y., 1935, p. 25.

(5) Rupp and Muller, *Z. anal. Chem.*, **67**, 20-23 (1925).