[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

The Mechanism of the Esterification of Strong Organic Acids. The Esterification of Neopentyl Alcohol with the Chloroacetic Acids[1,2]

BY OSBORNE R. QUAYLE AND HARRY M. NORTON[3]

The origin of the hydrogen and hydroxyl groups which form water in esterification has been the subject of much investigation. Since the work of Reid[4,5] with the sulfur analogs of both alcohols and acids, it has been conceded that in the case of weak organic acids the hydrogen only is from the alcohol. This has been confirmed by the esterification of methyl alcohol containing a high percentage of heavy oxygen.[6] The question has remained as to whether the course of the reaction with strong organic acids is the same or whether these acids provide only the hydrogen, acting similarly to the strong mineral acids such as hydrochloric.

Neopentyl alcohol was esterified with a series of carboxylic acids varying widely in strength.

TABLE I

EXPERIMENTAL DATA

Neopentyl ester	Yield after purif., %	Cl anal., % Calcd.	Found	$n^{20}D$	d^{20}_4	d^{30}_4	d^{40}_4	B. p. at 760 mm., °C.
Acetate	55			1.3893	0.8544	0.8444	0.8346	127
Chloroacetate	52	21.56	21.47	1.4211	1.0286	1.0177	1.0076	180
Dichloroacetate	50	35.63	35.71	1.4324	1.1311	1.1203	1.1107	194
Trichloroacetate	43	45.56	45.34	1.4373	1.2142	1.2024	1.1909	202
								M. p., °C.
p-Nitrobenzoate								54.0–54.5
3,5-Dinitrobenzoate								90.0–90.5

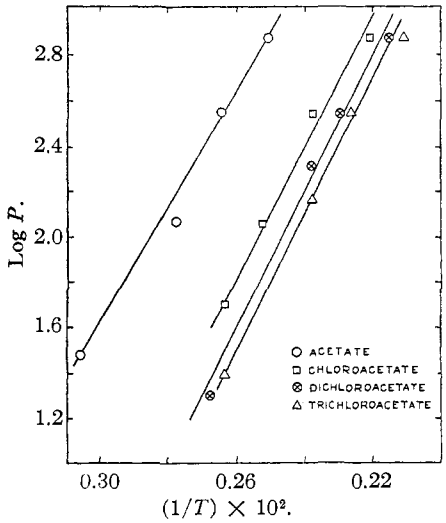

Fig. 1.—Vapor pressure of neopentyl esters.

This alcohol was chosen because of its unique property of rearranging if the electronic structure $CH_3:\ddot{C}:\ddot{C}:H$ (with CH_3 and H on the second carbon) is destroyed.[7,8,9,10] The removal of the hydroxyl group would break this structure; the removal of only hydrogen would not. Rearrangement of the neopentyl system yields *t*-amyl derivatives and is accompanied by the formation of unsaturated derivatives.

The neopentyl esters were made of chloroacetic, dichloroacetic and trichloroacetic acids, in addition to that of acetic acid previously discussed by Whitmore.[7] These esters when treated with bromine in a quantitative manner showed no evidence of the unsaturation which accompanies rearrangement.

Small portions of each ester (10 g.) were saponified and the resulting alcohol was identified in each case as neopentyl alcohol. Identification was established by mixed melting point determinations on the original alcohol with the alcohol obtained on saponification and on the *p*-nitrobenzoate derivatives. Since neopentyl alcohol was obtained from each ester, the neopentyl con-

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(2) Abstracted from the thesis presented by Harry M. Norton to the Graduate School of Emory University in partial fulfilment of the requirements for the degree of Master of Science.

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(4) E. E. Reid, *Am. Chem. J.*, **43**, 489 (1910).

(5) L. S. Pratt and E. E. Reid, THIS JOURNAL, **37**, 1939 (1915).

(6) I. Roberts and H. C. Urey, *ibid.*, **60**, 2391 (1938).

(7) F. C. Whitmore, "Organic Chemistry," D. Van Nostrand, Inc., New York City, 1937, p. 128.

(8) G. Edgar, G. Calingaert and R. E. Marker, THIS JOURNAL, **51**, 1487 (1929).

(9) F. C. Whitmore and H. S. Rothrock, *ibid.*, **54**, 3431 (1932).

(10) F. C. Whitmore, *ibid.*, **54**, 3279 (1932).

figuration had been maintained throughout all esterifications and saponifications. The linkage between the oxygen and carbon of the alcohol had been maintained at all times and the mechanism of the reaction is the same regardless of the strength of the acid.

Experimental

The neopentyl alcohol was prepared by the Grignard reaction from *t*-butyl chloride and formaldehyde gas. The latter was prepared by heating paraformaldehyde dried *in vacuo* over concentrated sulfuric acid for five days. Satisfactory yields of the acetates were obtained by standard methods.

The esters were hydrolyzed by 25% potassium hydroxide. The alcohol produced in each case was dried and the *p*-nitrobenzoate and the 3,5-dinitrobenzoate were made. No depressions in mixed melting point determinations were found, indicating that the alcohol obtained upon saponification was in each case neopentyl alcohol.

Table I and Fig. 1 summarize the experimental data obtained.

Summary

Neopentyl acetate, chloroacetate, dichloroacetate and trichloroacetate have been prepared, hydrolyzed and the resulting alcohol identified as neopentyl alcohol. No evidence of any rearrangement of the neopentyl group was obtained.

The refractive index, specific gravity at three temperatures, and boiling points at four pressures have been determined for each of the esters prepared.

The melting points of the 3,5-dinitrobenzoate and the *p*-nitrobenzoate of neopentyl alcohol are reported.

The conclusions are drawn (1) that in the esterification of alcohols by carboxylic acids varying in strength from that of glacial acetic to that of trichloroacetic, the water removed is composed of the hydrogen from the alcohol and the hydroxyl from the acid; (2) that in the hydrolysis of these esters the rupture of the carbon–oxygen linkage occurs between the oxygen of the alcohol residue and the carbon of the acid group.

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The Action of Elementary Fluorine Upon Organic Compounds. VIII. The Influence of Dilution on the Vapor Phase Fluorination of Ethane[1]

BY DEWALT S. YOUNG, NOBUKAZU FUKUHARA AND LUCIUS A. BIGELOW

In a previous paper of this series[2] we have described the vapor phase fluorination of ethane, using the pure gases in progressively varying proportions. The chief products were carbon tetrafluoride and hexafluoroethane, together with some higher boiling, partially fluorinated material, the liquid volume of which never exceeded 30% of the total condensate. This paper presents the results obtained when the fluorine was diluted progressively with nitrogen. They showed that the yield of the desired fluoroethanes could be raised to 90% of the total condensate under appropriate conditions.

The fluorinations were run in a metal apparatus, over copper gauze, as described before,[2] except that nitrogen, measured by a flowmeter, was introduced into the fluorine line. Two reaction chambers were used in series at the three highest dilutions, and adequate precautions taken throughout to avoid back pressure. The products were subsequently rectified in a Booth–Podbielniak low temperature fractionating unit,[2] and the higher boiling constituents divided into a number of empirically chosen cuts, from which pentafluoroethane CF_3CHF_2, *sym*-tetrafluoroethane CHF_2CHF_2, and 1,1,2-trifluoroethane CHF_2CH_2F were later isolated. However, no mono- or difluoroethanes were found, even when the fluorine was highly diluted.

Since it is known that alkyl monofluorides such as ethyl fluoride tend to be unstable, and also that ethylene fluoride decomposes spontaneously at 0°,[3] it seemed possible that these compounds, if formed at all, might have been decomposed immediately over the catalyst at the temperature of the reaction zone. Granting this, the fluorination

(1) This paper has been constructed in part from portions of Mr. Young's Doctorate Thesis, presented to the Graduate School of Duke University in October, 1939.

(2) Calfee, Fukuhara and Bigelow, THIS JOURNAL, **61**, 3552 (1939).

(3) Henne and Midgley, *ibid.*, **58**, 882, 884 (1936).