[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

Replacement Series of the Alkyl Groups as Determined by Alcoholysis of Esters

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It has seemed of interest to determine the relative replacing power of various alkyl groups in the alcoholysis of esters, *i. e.*

$$R'OH + RCO_2R'' \rightleftharpoons R''OH + RCO_2R'$$

as thereby a replacement series for the alkyl radicals may be constructed similar to the familiar one for the metals. Presumably the replacement series for the alkyl groups could be calculated from a knowledge of the extent of reaction of a given acid with a series of alcohols, *i. e.*

$$R'OH + RCO_2H \rightleftharpoons RCO_2R' + H_2O$$

However, accurate values for this latter system are not available for a large number of alcohols and even when obtained their relationship might be a function of the vagaries of aqueous solutions. Both reactions are being studied in this Laboratory but the present paper is concerned with the alcoholysis of esters.

Equilibrium has been established between various esters and alcohols by heating various proportions of the reactants at 200° in steel or glass for several hours. The extent of reaction has been determined by distilling off the lower boiling ester and alcohol under conditions which were demonstrated not to induce alcoholysis. The amount of the residual ester was then determined by saponification, and the proportions of the reactants at equilibrium and the value of K calculated. The constancy of the value of K obtained with variations in the proportions of the reactants was evidence that equilibrium conditions were attained. In certain cases equilibrium was established both from the "right" and the "left." A summary of the data obtained is given in Table I.

The data given in Table I for each set of reactants are based upon duplicate analyses of three or four equilibrium mixtures. Each set of reactants was run at both a ratio of 1 mole of alcohol per mole of ester and at 2 moles of alcohol per mole of ester. Approximately three-fourths of the equilibria mixtures were established in a steel bomb under a pressure of approximately 100 atm. of hydrogen. The remainder were in sealed glass tubes. Each reaction mixture contained as a catalyst 0.2 g. of water or 0.1 g. of aluminum ethoxide. The time required to reach equilibrium varied from less than two to 140 hours. Reaction was two or three times as rapid in steel under hydrogen as in glass. The time necessary for the establishment of equilibrium was ascertained by the trial and error method and was in general less than thirty-six hours in steel. The amounts of reactants used varied from 0.2 to 0.5 mole of ester and from 0.2 to 2.0 moles of alcohol. In general the volume of the reaction mixture in steel was 70 ml. or more and in some cases was as much as 150 ml.

The separation of the lower boiling ester from the higher boiling was carried out under a pressure of 2 to 30 mm. and at a temperature not in excess of 50°. In most cases the maximum temperature was not greater than 35°. The accuracy of the method and the absence of alcoholysis during distillation was proved by the distillation and analysis of synthetic mixtures containing known amounts of esters.

The majority of the alcohols were prepared by drying and fractionating commercial products. Duodecyl alcohol was prepared by the hydrogenation (250°, 200 atm. over copper–chromium oxide) of a sample of ethyl laurate of high purity obtained through the kindness of Dr. Carl S. Marvel. Isopropyl, *s*-butyl and *n*-butyl alcohols were prepared by the hydrogenation of carefully

TABLE I

EQUILIBRATION OF VARIOUS ALCOHOLS AND ESTERS

Reactants		AcOR,[a] mole	K
R of ROH	R′ of AcOR′		
Me	Duodecyl	0.543	1.43 ± 2
Et	Duodecyl	.491	0.92 ± 2
n-Pr	Duodecyl	.484	.86 ± 3
s-Pr	Duodecyl	.394	.42 ± 1
Allyl	Duodecyl	.424	.54 ± 2
n-Bu	Duodecyl	.488	.91 ± 4
i-Bu	Duodecyl	.440	.61 ± 1
s-Bu	Duodecyl	.386	.39 ± 1
Me	Benzyl	.628	2.86 ± 6
Et	Benzyl	.579	1.89 ± 4
Et	*n*-Heptyl	.478	0.85 ± 2
Et	Cyclohexyl	.585	2.05 ± 5
Et	2-Octyl	.542	1.37 ± 3
Et	3-Ph-propyl	.496	0.98 ± 2
Et	2-Ph-ethyl	.551	1.51 ± 5

[a] Average number of moles at equilibrium calculated, from the values of K, for a reaction mixture having originally 1 mole of ROH and 1 mole of AcOR′.

purified samples of the corresponding ketones and aldehyde. The esters were made through the reaction of an alcohol with acetic anhydride. The refractive indices and densities of the various alcohols were determined accurately and are given in Table III. The boiling ranges are also given but no special claim is made for their correctness as they were determined in a fractionating column with an ordinary thermometer without special precautions.

A numerical comparison of the relative reactivities of various alcohols in alcoholysis may be made in several ways upon the basis of the figures given in Table I. Thus for a given system the values of K constitute a basis of comparison. However, this method does not permit one to compare the replacing power of alcohols whose reactivities were measured in different systems. Since methanol has the greatest replacing power of any alcohol so far encountered, it seems convenient to use it as the basis of comparison. For example, when equimolecular quantities of methanol and duodecyl acetate react until equilibrium is attained the ratio of the esters present is 0.543 mole of methyl acetate/0.457 mole of duodecyl acetate or 1.19. For isopropyl alcohol the corresponding ratio is 0.65 (0.394/0.606), and for duodecyl 1. If these quotients are divided by 1.19, the relative reactivities are 1.00 for methyl, 0.55 for isopropyl, and 0.84 for duodecyl. The relative reactivity of methyl to ethyl was 1.09 in the duodecyl and 1.11 in the benzyl system, so that the figure 1.1 was used for transferring relative reactivities to the methyl basis for those systems in which ethyl and not methyl was used. The relative reactivities calculated for the various alkyl groups are given in Table II, column 2.

TABLE II

RELATIVE REACTIVITY OF ALKYL GROUPS IN ALCOHOLYSIS OF ACETATES

R	Relative reactivity	K^a	Log_{10} $K \times 100$
Methyl	1.00	1.00	0
Heptyl	0.90	0.81	− 9
Duodecyl	.84	.71	−15
3-Phenylpropyl	.83	.69	−16
Ethyl	.81	.66	−18
n-Butyl	.80	.64	−19
n-Propyl	.79	.62	−20
2-Octyl	.68	.46	−33
i-Butyl	.66	.44	−36
2-Ph-ethyl	.65	.42	−37
Allyl	.62	.38	−42
Benzyl	.59	.35	−46
s-Propyl	.55	.30	−52
Cyclohexyl	.55	.30	−52
s-Butyl	.53	.28	−55

[a] These are the equilibrium constants calculated for the reaction $ROH + AcOMe \rightleftharpoons AcOR + MeOH$.

These figures make it possible to calculate the concentrations at equilibrium of any two alcohols in the alcoholysis of their acetates. For example, if equimolecular amounts of *n*-butyl alcohol and benzyl acetates were allowed to react

$$\overset{1-x}{n\text{-}C_4H_9OH} + \overset{1-x}{C_6H_5CH_2OAc} \rightleftharpoons \overset{x}{n\text{-}C_4H_9OAc} + \overset{x}{C_6H_5CH_2OH}$$

at equilibrium there would be x moles of benzyl alcohol formed, and $1-x$ moles of *n*-butyl alcohol remaining in the system. The ratio of these two molar amounts will then be the ratio of their reactivities. Thus

$$\frac{x}{1-x} = \frac{59}{80}, \text{ or } x = 0.425 \text{ mole, and } 1 - x = 0.575 \text{ mole}$$

TABLE III

PROPERTIES OF REAGENTS

Reagents (alcohols)	B. p., °C.	n_{25}	d_4^{25}
Duodecyl	140–141 12	1.4415	(m. p. 24°)
Methyl	66	1.3270	0.7866
Ethyl	78	1.35944	.78517
n-Propyl	97	1.3835	.7999
i-Propyl	82	1.3748	.7806
n-Butyl	117	1.3973	.8056
i-Butyl	106	1.3939	.....
s-Butyl	99.5	1.39495	.8025
Allyl	95.7	1.4120	.8478
Benzyl	202–202.5	.....	1.0414
3-Ph-propyl	231–232	.....	0.9977
n-Heptyl	172–173	1.4235	.8223
Cyclohexyl	156.5–157	1.4642	.9444
Octanol-2	186.5–187.5	1.4230	.81555
2-Ph-ethyl	213–214	.....	1.0198

(Acetates)		Saponification equivalents Calcd.	Found (Av.)
Duodecyl	142–143 6	228	226.5
Benzyl	98 14	150	151.5
3-Ph-propyl	136 21	178	180
n-Heptyl	185–187	158	162
Cyclohexyl	171–173	142	144.5
2-Octyl	193–194.5	172	174
2-Ph-ethyl	225–226	164	164
Ethyl	76.5	88	88

The differences between alkyl groups probably can be brought out more truly by considering the equilibrium constants calculated from the relative reactivities. These constants, for the reaction where a given alcohol replaces methyl, are readily calculated as follows. Starting with equimolar amounts, in the system

$$\overset{1.00}{n\text{-}BuOH} + \overset{1.00}{AcOMe} \rightleftharpoons \overset{0.80}{AcOBu} + \overset{0.80}{MeOH}$$

at equilibrium the amounts of butyl alcohol and methyl alcohol which are present will bear the same ratio to each other as the inverse ratio of their reactivities. The equilibrium constant is then given by

$$K = \frac{0.80 \times 0.80}{1.0 \times 1.0} = 0.64$$

In other words, K in each case is the square of the relative reactivity value. The logarithms of K (x 100) given in the last column of Table II are perhaps the fairest measure of the differences in chemical reactivity of the alkyl group in alcoholysis.

From the relative reactivities, however calculated, certain general conclusions may be drawn. The substitution of any group for a hydrogen of methyl results in reduction in reactivity. The primary straight chain alkyl groups are similar and show comparatively small difference, yet there can be no question that *n*-heptyl is distinctly more reactive than *n*-propyl. A branching of the chain, or the presence of an unsaturated linkage adjacent to the carbinol, distinctly lowers the reactivity of an alcohol. The simple secondary alcohols show decidedly lower reactivity than do the primary alcohols but octanol-2, as in the acetal reaction, is distinctly more reactive than certain primary alcohols.

It is not worth while at the present time to make a comparison between Menschutkin's figures upon the extent of the ester reaction with various alcohols and the extent of alcoholysis in systems involving these same alcohols except to say that the relative reactivities are similar in the two systems.[1]

It should be pointed out that the statement given in various textbooks that secondary alcohols react to the extent of only 40 to 50% to form an ester with an equimolecular amount of acetic acid is not correct and is based upon a misreading of Menschutkin's papers. He really gave the figures 60.3% for isopropyl and 59.3 for *s*-butyl at 155°. Measurements in this Laboratory gave a value of about 58% for isopropyl at 200°.

It is interesting to note that the relative replacing power of hydrogen for methyl is 0.44 calculated upon the basis of the concentrations at equilibrium as given by Menschutkin for the reaction

$$\overset{0.305}{\mathrm{HOH}} + \overset{0.305}{\mathrm{MeOAc}} \rightleftharpoons \overset{0.695}{\mathrm{AcOH}} + \overset{0.695}{\mathrm{MeOH}}$$

The figure 0.44 for hydrogen is distinctly lower than that for any alkyl group given in Table II, but considerably higher than those for phenyl or *t*-butyl. One may then say that primary and secondary alkyl groups are more reactive while tertiary groups are less reactive in alcoholysis than hydrogen.

Summary

The extent of replacement of one alkyl group by another in the alcoholysis of various acetates has been ascertained. The relative replacing powers of fourteen alkyl groups referred to methyl have been calculated and recorded in Table II.

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[1] Menschutkin, *Ber.*, **11**, 1507 (1878); *Ann.*, **197**, 193 (1879); *Ann. chim. phys.*, [5] **23**, 14 (1881); *ibid.*, [5] **30**, 81 (1883).

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The Nitro and Amino Derivatives of *t*-Butylbenzene

By David Craig

In connection with studies involving certain aromatic amines it became necessary to investigate the nitration[1,2,3,4,5] of *t*-butylbenzene. The rather meager work reported in this field is in some cases conflicting and is entirely inadequate from the viewpoint of the preparation of *o*-nitro-*t*-butylbenzene. Accordingly it seems well to report the following studies which confirm and extend the early investigations of Senkowski.

t-Butylbenzene when nitrated is found to give a mixture of about 77% of *p*-nitro-*t*-butylbenzene with about 23% of the ortho isomer.[6] The presence of *m*-nitro-*t*-butylbenzene[7] was not noticed although it may have been present in small amounts. The use of mixed acid at room temperature is satisfactory for the nitration, a fact which does not seem to have been recognized thus far.

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[1] Senkowski, *Ber.*, **23**, 2412 (1890).

[2] Baur, *ibid.*, **27**, 1610 (1894).

[3] Henderson and Boyd, *J. Chem. Soc.*, **97**, 1665 (1910).

[4] Malherbe, *Ber.*, **52**, 319 (1919).

[5] Shoesmith and Mackie, *J. Chem. Soc.*, 2334 (1928).

[6] Under the same conditions of nitration the amount of para substitution increased with different alkylbenzenes in the following order: methyl, ethyl, isopropyl, *t*-butyl. See (a) Le Fèvre, *ibid.*, 981 (1933); (b) Brady *et al.*, *ibid.*, 114 and 121 (1934).

[7] Gelzer, *Ber.*, **21**, 2947 (1888).