

639. *The Rearrangement of $\alpha\beta$ -Unsaturated Alcohols to Saturated Aldehydes and Ketones. Part II.* The Course of the Rearrangement.*

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The rates of change of a number of $\alpha\beta$ -unsaturated alcohols into carbonyl compounds are compared with those of the corresponding 1 : 2-glycols, and a hypothesis to account for the observed results is developed.

IN order to follow the change of an unsaturated alcohol or a 1 : 2-diol into a carbonyl compound a rapid and reliable method of estimating aldehydes and ketones in dilute solution was necessary. Several methods were tested against *isobutyraldehyde* and methyl *isopropyl ketone*. 2 : 4-Dinitrophenylhydrazine¹ or dimedone² did not give reproducible results. Modifications of Ripper's bisulphite method³ and of Romijn's alkaline iodine method⁴ were also unsuitable. Accurate and reliable results were obtained with the silver oxide method⁵ but it was time-consuming. Eventually a colorimetric method based on the use of Schiff's reagent was adopted for the estimation of aldehydes. For ketones, Mitchell and Smith's hydroxylamine method⁶ proved satisfactory provided that comparison was made with reference samples.

The rates of change of 2-methylprop-2-en-1-ol and of 2-methylpropane-1 : 2-diol into *isobutyraldehyde* in presence of sulphuric acid were determined in water-dioxan (3 : 1 v/v), at $90^\circ \pm 0.1^\circ$. The observed values of *k*, the first-order rate constant, are shown in Table I. The rearrangements of unsaturated alcohol and the glycol are obviously both first-order

* Part I, preceding paper.

¹ Iddles *et al.*, *Ind. Eng. Chem. Anal.*, 1939, **11**, 102.

² Yoe and Reid, *ibid.*, 1941, **13**, 238.

³ Goldman and Yagoda, *ibid.*, 1943, **15**, 377; Ripper, *Monatsh.*, 1900, **21**, 1039.

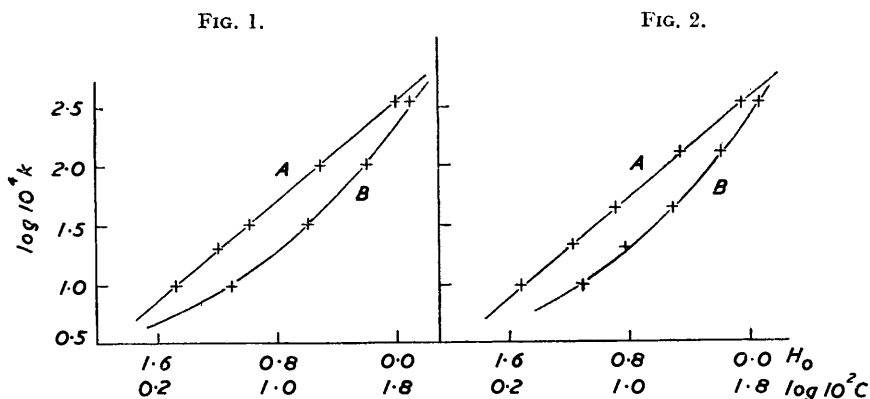
⁴ Romijn, *Z. analyt. Chem.*, 1897, **36**, 18; Siggia and Maxcy, *Analyt. Chem.*, 1947, **19**, 1023.

⁵ Mitchell and Smith, *ibid.*, 1950, **22**, 746.

⁶ *Idem, ibid.*, p. 752.

reactions, although the rate constant decreases after about 80% conversion, presumably owing to intervention of side-reactions. Table 2 shows that the rate constants are independent of the initial concentration of the alcohol or glycol over the range 0.02—0.15 mole/l. At higher concentrations, where the compound formed an appreciable part of the reaction mixture, there was a significant decrease.

The rate constants in various strengths of sulphuric acid for 0.05 mole/l. solutions of 2-methylprop-2-en-1-ol, 2-methylpropane-1 : 2-diol, 3-methylbut-3-en-2-ol, and 2-methylbutane-2 : 3-diol are shown in Table 3. The rate constants are proportional to Hammett's acidity function (Figs. 1 and 2).



Relation of rate constant and Hammett's acidity function for (FIG. 1) 2-methylprop-2-en-1-ol and (FIG. 2) 2-methylpropane-1 : 2-diol (both 0.05 mole/l.) under the standard conditions.

A, $\log 10^4 k - H_0$. B, $\log 10^4 k - \log 10^2 C_A$.

The rate constants for the series of unsaturated alcohols $\text{CH}_2\text{:CR}\cdot\text{CH}_2\cdot\text{OH}$ and the corresponding glycols $\text{CH}_2\text{:CR(OH)}\cdot\text{CH}_2\cdot\text{OH}$ are shown in Table 4 and for the alcohols $\text{CH}_2\text{:CMe}\cdot\text{CHMe}\cdot\text{OH}$, $\text{CH}_2\text{:CMe}\cdot\text{CHEt}\cdot\text{OH}$, and $\text{CHEt}\cdot\text{CMe}\cdot\text{CHEt}\cdot\text{OH}$ in Table 5.

TABLE 1. Values $10^4 k$ (min.^{-1}) for changes with 2% w/v sulphuric acid in dioxan-water (1 : 3 v/v) at $90^\circ \pm 0.1^\circ$.

Time (hr.)	1	2	3	4	6	8	10	Mean *
$\text{CH}_2\text{:CMe}\cdot\text{CH}_2\cdot\text{OH}$								
Concn., 0.0587 mole/l.	37.6	36.3	41.7	37.4	39.8	34.2	31.6	38.6
„ 0.0613 „	35.1	37.8	35.5	40.1	36.2	33.8	30.5	36.9
„ 0.0736 „	40.7	37.6	41.2	37.9	38.6	32.1	32.0	39.2
$\text{HO}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$								
Concn., 0.0561 mole/l.	41.6	43.8	39.2	42.8	40.3	35.6	31.8	41.6
„ 0.0629 „	44.8	42.2	41.3	39.1	43.7	32.3	33.1	42.2
„ 0.0752 „	38.8	40.4	42.1	39.6	40.2	34.1	30.1	40.1

* Only the first five results were used in calculating the mean.

TABLE 2. Effect of initial concentration on $10^4 k$ (min.^{-1}) with 2% w/v sulphuric acid in dioxan-water (1 : 3 v/v) at $90^\circ \pm 0.1^\circ$.

Concn. (mole/l.)	$\text{CH}_2\text{:CMe}\cdot\text{CH}_2\cdot\text{OH}$	$\text{HO}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$	$\text{CH}_2\text{:CMe}\cdot\text{CHMe}\cdot\text{OH}$	$\text{HO}\cdot\text{CMe}_2\cdot\text{CHMe}\cdot\text{OH}$
0.020	38.4	40.6	18.6	21.3
0.050	39.6	42.2	19.1	20.6
0.075	37.1	40.1	17.8	21.1
0.10	38.8	39.6	18.3	22.4
0.15	36.8	41.8	19.2	20.8
0.20	34.6	38.0	16.8	18.3
0.30	32.1	36.5	15.4	18.8
Mean *	38.2	40.8	18.6	21.2

* Only the first five results were used to determine the mean.

TABLE 3. *Effect of sulphuric acid concentration on 10^4k (min.^{-1}) in dioxan-water (1 : 3 v/v) at $90^\circ \pm 0.1^\circ$. The initial concentration of alcohol or glycol at 0.05 mole/l.*

H_2SO_4 (% w/v)	$\text{CH}_2:\text{CMe}\cdot\text{CH}_2\cdot\text{OH}$	$\text{HO}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ *	$\text{CH}_2:\text{CMe}\cdot\text{CHMe}\cdot\text{OH}$	$\text{HO}\cdot\text{CMe}_2\cdot\text{CHMe}\cdot\text{OH}$ †
0.5	9.30	10.0	4.45	5.45
1.0	19.9	21.1	9.70	10.2
2.0	38.2	40.8	18.6	21.2
5.0	132	132	63.1	72.5
10.0	417	392	198	229

* Harvey, Riggs, and Stimson (*J.*, 1955, 3267) found $10^4k = 90$ in 1.2% w/v acid at 97° .

† Suter and Zook (*J. Amer. Chem. Soc.*, 1944, **66**, 738) found $10^4k = 1.2$ in 0.5% w/v acid at 80° .

TABLE 4. *Values of 10^4k for a series of unsaturated alcohols and the corresponding glycols, under standard conditions.*

R	H	Me	Et	Pr	Pr ^t	Bu	Bu ^t
$\text{CH}_2:\text{CR}\cdot\text{CH}_2\cdot\text{OH}$	ca. 0.02	38.2	30.4	23.6	23.6	29.4	16.4
$\text{HO}\cdot\text{CMeR}\cdot\text{CH}_2\cdot\text{OH}$	ca. 0.02	40.8	34.1	30.6	27.4	31.9	19.9

TABLE 5. *Values of 10^4k for some alcohols (0.05 mole/l.) with 10% w/v sulphuric acid in dioxan-water (3 : 1 v/v) at $90^\circ \pm 0.1^\circ$.*

$\text{CH}_2:\text{CMe}\cdot\text{CH}_2\cdot\text{OH}$, 417;	$\text{CH}_2:\text{CMe}\cdot\text{CHMe}\cdot\text{OH}$, 198;
$\text{CH}_2:\text{CMe}\cdot\text{CHEt}\cdot\text{OH}$, 185;	$\text{CHEt}\cdot\text{CMe}\cdot\text{CHEt}\cdot\text{OH}$, 1.82

EXPERIMENTAL

Estimation of Aldehydes.—A solution of the appropriate pure aldehyde in water-dioxan containing sulphuric acid was diluted to give reference samples containing 100, 75, 50, and 25% of the calculated amount of reaction product. The 100% sample was treated with a standard amount of Schiff's reagent, kept at 25° until the colour was well-developed and then examined in a Unicam photoelectric spectrophotometer to determine the wavelength of maximum absorption and the most suitable dilution. The reference samples and the samples from a reaction run were then diluted with water, treated with Schiff's reagent, and stored at 25° for a fixed period, and absorption at the selected wavelength measured. The method was independent of daily variation of conditions since each set of products was always compared with its own set of reference samples.

Determination of Reaction Rates.—A weighed sample of the unsaturated alcohol or glycol was added to the requisite amount of dioxan-water (1 : 3 v/v) containing sulphuric acid in a flask with a capillary tap run-off heated at $90^\circ \pm 1^\circ$. The contents of the flask were quickly shaken and, at intervals, the flask was quickly removed from the bath and a small sample taken and cooled rapidly to 0° . A measured sample was then pipetted out and diluted, and the content of aldehyde or ketone determined.

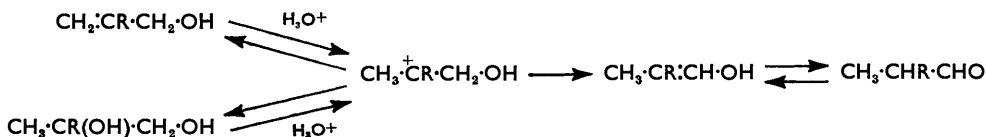
In each run five values of k were determined in the time range corresponding to 20–75% of rearrangement. The agreement between the values of k in a single run appeared to be about $\pm 10\%$; the error in the mean value of k was probably not more than $\pm 5\%$.

DISCUSSION

A comparison of the rates of formation of carbonyl compounds from $\alpha\beta$ -unsaturated alcohols and from the corresponding glycols shows that both groups are influenced in the same way by alkyl substituents (Tables 4 and 5). Allyl alcohol and propane-1 : 2-diol yield propionaldehyde very slowly; the introduction of an alkyl group into the β -position enormously facilitates prototropic change whereas the presence of alkyl groups in other positions hinders it.

The close resemblance between the unsaturated alcohols and the corresponding glycols in behaviour towards dilute acid cannot be accidental and strongly suggests that there is some intermediate common to both sets of changes. If the commonly accepted view of the course of the conversion of 1 : 2-glycols into carbonyl compounds is assumed, the

prototropic change of $\alpha\beta$ -unsaturated alcohols and the change of 1:2-glycols can be formally represented as shown.

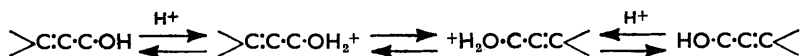


If this is true, a major feature determining the facility of prototropic change is the basic character of the γ -carbon atom since attachment of a proton to this atom is a necessary condition for validity of the hypothesis of a common intermediate. There can be no doubt that the unsaturated alcohol has a basic function since the observed rate constants are proportional to Hammett's acidity function which as a measure of the tendency of a reaction medium to donate a proton to a neutral base.

On this basis, the effect of an alkyl group on the β -carbon atom in promoting prototropic change is explicable, as also is the retarding influence of an alkyl group on the γ -carbon atom. An alkyl group on the α -carbon atom would also be expected to retard prototropic change by increasing the basicity of the hydroxyl group at the expense of the γ -carbon atom.

Any hypothesis of prototropic change must also permit a satisfactory explanation of oxotropy and dehydration both of which are proton catalysed and, as shown in this work, may occur simultaneously under the same conditions. It is clear from the work of Braude *et al.*⁷ that the facility of oxotropy is influenced to a considerable extent by structural effects. In the system $\text{RCH}\text{:CR}'\cdot\text{CHR}''\cdot\text{OH}$ the change is favoured when $\text{R} = \text{alkyl}$ and suppressed if $\text{R}' = \text{alkyl}$; that is, the structural effects which favour prototropic change are those which retard oxotropy and conversely.

The initiating phase of the transfer of the hydroxyl group from $\text{C}_{(\alpha)}$ to $\text{C}_{(\gamma)}$ is the addition of a proton to the hydroxyl group. Oxotropy change may, therefore, be represented:



The relative basicities of the hydroxyl group and the γ -carbon atom are the criteria which determine whether prototropy or oxotropy is the main reaction and control the composition of the final product. It is also clear that the factor which determines whether or not prototropy can occur is the presence of structural features which provide a reaction path of sufficiently low energy. The nature of this effect can be deduced from the variation of the rate of change with the nature of the alkyl group on the β -carbon atom (Table 4). The activating influence falls off in the order $\text{Me} > \text{Et} > \text{Pr}^i > \text{Bu}^t$ which is quantitatively the same as the order of contribution of these groups in hyperconjugation.⁸ The ratio of the effect $\text{Me} : \text{Et} : \text{Pr}^i : \text{Bu}^t = 1.0 : 0.8 : 0.62 : 0.43$ is similar to that observed by Hughes and Ingold⁹ in the hydrolysis of substituted diphenylmethyl chlorides, namely $\text{Me} : \text{Et} : \text{Pr}^i : \text{Bu}^t = 1.0 : 0.75 : 0.56 : 0.43$.

It is, therefore, clear that whereas alkyl groups attached to the α - and the γ -carbon atom exert merely their normal inductive effect on the polarisation of the molecule, alkyl groups on the β -carbon atom exert a dynamic time-variable effect on the polarisability of the molecule. For this reason, the effect of an alkyl group on the β -carbon atom is to increase the rate of prototropic change by a factor of about 2000, whereas alkyl groups on the α - and the γ -carbon atom decrease the rate by a factor of 2—100.

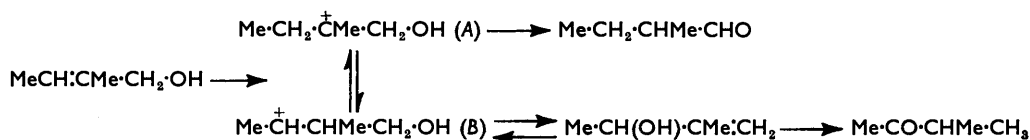
⁷ Braude and Jones, *J.*, 1946, 122; Braude and Timmons, *J.*, 1950, 2000.

⁸ See Crawford, *Quart. Rev.*, 1949, 3, 226.

⁹ Hughes and Ingold, *J.*, 1940, 949.

This substantial effect of an alkyl group on the β -carbon atom in facilitating acid-catalysed prototropic change in a three-carbon system has been observed previously; Linstead, Kon, and their co-workers¹⁰ found that the compounds $>C=C-CHX$, where $X = CO_2H$, COR , or CO_2Et , undergo acid-catalysed prototropic change only if the β -carbon atom carries an alkyl group.

In the unsaturated alcohols $CH_2:CR\cdot CH_2\cdot OH$ oxotropic change could occur without being detected, but observations on the secondary alcohols $CH_2:CR\cdot CHR'\cdot OH$ make this improbable. The product from these alcohols is almost exclusively the ketone (90%), and an aldehyde, which would result from oxotropic change followed by prototropy, is present only in small amount. With the alcohols $RCH:CR'\cdot CH_2\cdot OH$ concurrent oxotropy and prototropy is more evident (Part I, Table 4). A possible explanation of simultaneous oxotropy and prototropy is that the capacity of the γ -carbon atom to accept a proton is reduced by the presence of the alkyl substituent and consequent competition with the β -carbon atom. Such alcohols in acid solution can then give rise to two species (*A*) and (*B*) in equilibrium and both present in appreciable amounts.



This view is reinforced by the observation that alcohols having two $C_{(\gamma)}$ methyl groups do not undergo prototropic change. Instead they are dehydrated to dienes. It would seem as if oxotropic change occurred:



As well as similarity between the prototropic changes of $\alpha\beta$ -unsaturated alcohols and the rearrangement of 1:2-glycols, there are some differences. In particular, the $\alpha\beta$ -unsaturated alcohols $CH_2:CH\cdot CR_2\cdot OH$ and $CMe_2:CMe\cdot CH_2\cdot OH$ are dehydrated under the conditions used. The corresponding glycols $CH_3\cdot CH(\text{OH})\cdot CR_2\cdot OH$ and $CHMe_2\cdot CMe(\text{OH})\cdot CH_2\cdot OH$ however are rearranged smoothly to the corresponding carbonyl compounds. These exceptions are simply explained on our hypothesis: these unsaturated alcohols have as their most basic point the hydroxyl group, and consequently the carbonium ion is not formed to any extent. Instead oxotropic change and dehydration is the predominant reaction.

Less striking differences are the formation of small amounts of aldehyde from $Me_2C(\text{OH})\cdot CHMe\cdot OH$ and $EtCMe(\text{OH})\cdot CHEt\cdot OH$ together with the ketone: the corresponding unsaturated alcohols give only the ketone and *no* aldehyde. An obvious explanation is that, in the glycol, both hydroxyl groups are liable to be split out to give the intermediate carbonium ion, with the result that two carbonium species are intermediates in the reaction. The relative proportion of each will obviously depend on the basicity of each hydroxyl group.

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¹⁰ *J.*, 1925, 616; 1926, 2748; 1928, 1630; 1931, 248; 1934, 623.