

XXXII.—*Catalytic Influences in Three-carbon Tautomerism. Part II. The Action of Acid Catalysts on Ketones.*

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IN Part I (J., 1929, 1269) a detailed study was made of the conversion of *cyclohexylideneacetone* and its $\beta\gamma$ -isomeride into an equilibrium mixture of the two under the influence of sodium alkyloxides, and it was shown that the change can be approximately represented as a unimolecular reversible reaction, although a side reaction, consisting in the addition of the elements of alcohol, could be detected. The order of activity of different sodium alkyloxides agrees with the prediction based on an ionic mechanism of the change, involving the separation of a proton under the influence of the catalyst (alkyloxide ions).

Acid catalysts (hydrogen ions) also are capable of promoting prototropic change, although they are less effective than alkaline catalysts (Lowry and Richards, J., 1925, 127, 1371; Baker, J., 1928, 1584), the difference in activity being generally attributed to the indirect action of hydrogen ions in bringing about the separation of the proton necessary for the change (compare Ingold and Shoppee, J., 1929, 1199).

It is therefore to be expected that acids would promote, for example, the interconversion of *cyclohexylidene-* and *cyclohexenyl-acetone*. Moreover, if the equilibrium between these compounds is a true structural constant, the equilibrium mixture obtained with the aid of acid catalysts must have the same composition as that produced by alkaline reagents. It might also be expected that acids would be less active in promoting the change, their relative activity depending on their strength.

Indications of the activity of acids in causing interconversion of ketones have frequently been noted; *e.g.*, many ketones cannot be regenerated from their semicarbazones or oximes by the action of hot aqueous acids (Hugh, Kon, and Linstead, J., 1927, 2585), and some acids cannot be esterified without extensive isomerisation in boiling alcohol containing a mineral acid (unpublished observation).

The action of sulphuric, hydrochloric, and oxalic acids on *cyclohexylidene-* and *cyclohexenyl-acetone* and on *isopulegone* has now been investigated. The acids are less rapid in their action than the catalysts previously employed; *e.g.*, *N*-aqueous-alcoholic sulphuric acid at 25° produces only 22% change in *cyclohexylideneacetone* in 4 hours, which is equivalent to about 4 minutes' treatment with

N-sodium ethoxide. Longer treatment gives rise to extensive side-reactions (addition); at 100°, however, isomerisation proceeds smoothly and side reactions are negligible in the time required to reach equilibrium. Heating for $\frac{1}{2}$ hour is sufficient to produce the same equilibrium mixture from either ketone by means of *N*-aqueous-alcoholic sulphuric acid. With hydrochloric acid, the same equilibrium point is reached, but side reactions occur more readily and a chlorine-containing high-boiling fraction is obtained. Oxalic acid is much slower in its action.

The earlier experiments were performed with a sample of *cyclohexylideneacetone* similar to that used in the previous investigation and the equilibrium mixture produced from it had all the properties and the composition, as ascertained by Linstead and May's iodometric method (J., 1927, 2565), of the equilibrium mixtures obtained with the aid of alkaline catalysts (addition about 75%, corresponding to 30% $\alpha\beta$). The $\beta\gamma$ -ketone consistently gave equilibrium mixtures richer in the $\beta\gamma$ -form, as indicated by a higher addition of iodine chloride (78—80%); a similar discrepancy was noticed during the previous research, but the significance of the two isolated experiments with sodium propoxide and *isopropoxide* was not then apparent and the results were thought to be accidental. It has now been found that when pure *cyclohexylideneacetone*, which has only lately become available (Kon, J., 1930, 1616), is employed, the equilibrium mixture obtained has the higher iodine addition (about 78%) together with the other properties of the product obtained from the $\beta\gamma$ -ketone with the aid of acid catalysts or sodium propoxide and *isopropoxide*. The slightly lower value observed with *cyclohexylideneacetone* purified by distillation only is due to the presence of esters which it is impossible to remove by fractionation.

The new value for the point of equilibrium is 23% of $\alpha\beta$ -ketone. The experiments constitute strong evidence that the same point of equilibrium is reached both with acid and with alkaline catalysts and that this therefore represents a true structural constant.

isoPulegone is rapidly isomerised to *pulegone* by hot alcoholic sulphuric acid (there appears to be no hydrolysis to acetone and 3-methyl*cyclohexanone* under the conditions employed), the point of equilibrium being coincident, within the limits of the experimental error, with pure *pulegone*. Although *pulegone* is readily isolated from the equilibrium mixture in the form of semicarbazone, its physical properties differ somewhat from those of pure *pulegone*, and it may be that the equilibration of *isopulegone* is a less simple process than hitherto supposed.

The equilibration of *isopulegone* with sodium ethoxide under the standard conditions developed in Part I was complete at the end of

5 minutes and therefore no estimate of the mobility was possible. In view of this high mobility it is all the more surprising that *isopulegone* survives the process of preparation from *isopulegol* by oxidation with hot dichromate in the presence of sulphuric acid without appreciable conversion into *pulegone*.

EXPERIMENTAL.

Materials.—*cycloHexylideneacetone* was prepared as described by Dickins, Hugh, and Kon (J., 1928, 1630) and purified by repeated fractionation; in a few experiments, marked *, the pure ketone regenerated as described by Kon (*loc. cit.*) was employed. The *cyclohexenylacetone*, *isopulegone*, and *pulegone* were also pure specimens regenerated by that method.

Procedure.—The acids used were normal, the sulphuric acid employed in the preliminary work (Experiments 2—6) being made by diluting 50% (by volume) aqueous acid with 96% alcohol; later, aqueous 2.195*N*-acid was diluted to normality with 96% alcohol just before use (Experiments 9—14). The hydrochloric acid was made by diluting pure hydrochloric acid (33%) with 96% alcohol. The oxalic acid was 1.983*N* in 90% alcohol.

Except in the experiments at room temperature or at 25°, the mixture of ketone with the calculated amount of acid was sealed up in a glass tube and heated in boiling water for the requisite time; it was then rapidly cooled and poured into water to arrest the action.

The method of isolation and analysis was that given in Part I. The physical properties of the product were determined as a check but are not recorded. The equilibrium mixtures obtained by the action of sulphuric acid on *cyclohexylideneacetone* and *cyclohexenylacetone* in 60 minutes were analysed (Found: from $\alpha\beta$, C, 77.6; H, 10.2; from $\beta\gamma$, C, 77.8; H, 10.2. Calc.: C, 78.1; H, 10.2%), the results showing that little or no addition of alcohol or water had taken place. For the iodometric analysis of *pulegone-isopulegone* mixtures a new reference curve was constructed from the following values:

% Pulegone	100	90	75	50	25	10	0
% Iodine addition	12.7	21.6	32.0	47.7	57.8	62.5	65.4

Results.—Expt. 1. *cycloHexylideneacetone* was mechanically shaken with a large excess of *N*-aqueous sulphuric acid for 3 days at room temperature. At first there was very little change; at the end of the period the refractive index of the ketone had dropped considerably but the iodine addition had only risen from 16.9 to 26.2%; the change in properties was therefore due to a side reaction such as

addition of water to the double bond and not to the formation of the $\beta\gamma$ -ketone. Other experiments are summarised below :

Expt.	Reagent.	Material.	Time (mins.).	% Iodine addition.	% $\alpha\beta$ -Ketone.
2	$N-H_2SO_4$ at 25°	$\alpha\beta$	480	38.1	78
3	" "	"	1080	53.4	61
4	" at 100°	"	90	75.1	29
5	" "	"	1020	55.8	—
6	" "	"	30	74.8	29
7	$2N-C_2H_2O_4$ at 100°	"	30	48.7	66
8	$N-HCl$ at 100°	"	30	75.1	29
9	$N-H_2SO_4$ at 100°	"	60	73.8	31
10	" "	"	60	74.5	30
11	" "	$\beta\gamma$	30	80.3	19
"	" "	"	60	80.3	19
12	" "	"	30	78.3	23
"	" "	"	60	78.7	22
13	" "	"	120	78.3	23
"	" "	$\alpha\beta^*$	30	78.6	22
14	" " in excess	" *	60	79.8	20
"	" "	$\beta\gamma$	60	77.9	24
"	" "	$\alpha\beta^*$	60	77.6	25
15	$NaOPr^a$ at 25°	$\beta\gamma$	360	77.9	24
16	$NaOPr^b$ at 25°	"	360	79.4	21
17	$N-H_2SO_4$ at 100°	<i>iso</i> Pulegone	30	12.7	100
18	$N-NaOEt$ at 25°	"	5	12.3	100
"	" "	"	10	12.2	"
"	" "	"	30	10.4	"
"	" "	"	60	10.1	"

The products of Expts. 3 and 5 each boiled over a range and a considerable high fraction was present. The iodine additions recorded refer to a fraction covering the boiling points of both ketones in every case.

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