ENOLISING ACTION OF HYDROGEN CHLORIDE ON ALDEHYDES AND KETONES[1]

By Vinayak Keshav Bhagwat.

The probable enolisation of ketones during the process of halogenation was first clearly pointed out by Lapworth[2] who studied the reaction in various solvents and drew the conclusion that the halogen is absorbed by the unsaturated modification of the ketone.

Dawson and his co-workers put forward a similar explanation of the mechanism of halogenation of acetaldehyde and its homologues.[3] They have further found that halogenation is accelerated in the presence of a strong acid such as hydrochloric or sulphuric acid. According to their view, the presence of a negative group in the molecule or of a catalyst in the reaction mixture promotes enolisation of the aldehyde and thus accelerates halogenation.

Up to the present, however, in only one instance have acetone and acetaldehyde been observed to react in the enolic form.[4]

Dr. Sudborough and the author found that simple aldehydes and ketones display very little tendency to enolise in the presence of Grignard's reagent[5] a moderately high degree of enolisation was observed, however, in the case of an acid sample of *iso*valeraldehyde, and the suggestion was made that this result might have been due to the enolising action of the acid. In view of the work of Dawson, the explanation seems satisfactory, but it must be remembered that the acid—presumably *iso*valeric acid—would decompose in presence of Grignard's reagent and therefore would have no chance to exert its enolising influence. It seems likely, therefore, that the marked enolisation in the case of the acid sample was due to the trace of water (formed in the auto-oxidation of the aldehyde) not having been removed by the calcium chloride.

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[1] Published in the *Journal of the Chemical Society*, 1923, **123**, 1803, under the title 'Influence of hydrogen chloride on the enolising action of Grignard's reagent.'

[2] *J. Chem. Soc.*, 1904, **85**, 30.

[3] *J. Chem. Soc.*, 1909, **95**, 1860; 1914, **105**, 275, 387.

[4] Freer, *Amer. Chem. J.*, 1890, **12**, 355; 1891, **13**, 319.

[5] *This Journal*, 1919, **2**, 192.

In order to settle this point, the present investigation was undertaken. The results corroborate the first view, for it was found that whilst acetic acid has no influence on the enolising action of Grignard's reagent, hydrogen chloride exerts a very great influence.

EXPERIMENTAL.

As slight variations of temperature affect the vapour pressure of ethyl-ethereal solutions to an appreciable extent, all the experiments were performed in pure *iso*amyl-ethereal solution as suggested by Hibbert and Sudborough.[1] To obviate the small errors due to the absorption of moisture, carbon dioxide, and oxygen, the apparatus was filled with pure dry nitrogen in each experiment.

The amyl ether was prepared from commercial *iso*amyl alcohol (b. p. 128-130°) by Schröter and Sontag's method[2] and purified by keeping over calcium chloride for about two days and then boiling twice with metallic sodium for eight hours, with intermediate distillation; it was thereafter successively treated with a little magnesium methyl iodide, sodium, and phosphoric oxide and finally distilled.

The Grignard's reagent was prepared as described by Hibbert and Sudborough, and the nitrogen by the method given by Lupton.[3]

Propaldehyde, prepared by Lieben's method[4] was repeatedly carefully fractionated, treated with calcium chloride, and again fractionated, until a product of constant density was obtained; b. p. 44·5-45·5°/687 mm.; d^{0} 0·8402.

*iso*Valeraldehyde, prepared by Bouveault and Rosset's method[5] was purified as above; b. p. 88·5-89·5°/684 mm., d^{0° 0·8212.

Merck's extra pure acetone was dehydrated with fused calcium chloride and distilled until the density was constant; b. p. 53·5°/688 mm., d^{25° 0·7849.

Pure glacial acetic acid, m. p. 16°, was used in these experiments. A dilute solution of hydrogen chloride in dry amyl ether was prepared and standardised by titrating with standard caustic soda the aqueous extract of a weighed quantity.

Small quantities of the acid solution and of the substance were weighed in a stoppered tube and then dissolved in about 10 c.c. of dry amyl ether. The tube containing the solution was lowered vertically into a stout filter flask of about 250 c.c. capacity, provided

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[1] *J. Chem. Soc.*, 1904, **85**, 934.

[2] *Ber.*, 1901, **41**, 1924.

[3] *Chem. News*, 1876, **33**, 90.

[4] *Monatsh.*, 1883, **4**, 14.

[5] *Bull. Soc. chim.*, 1894 [iii], **11**, 301.

with an air-tight rubber bung carrying a tapped tube nearly touching the bottom of the flask. Excess of magnesium methyl iodide solution (about 10-15 c.c.) having been placed in the flask, the air was displaced by nitrogen which had bubbled through concentrated sulphuric acid and passed over phosphoric oxide. The side tube of the flask was attached to a Lunge nitrometer filled with dry mercury, and the apparatus was left for one to two hours to attain room temperature. The level of the mercury in the nitrometer and the temperature having then been noted, the two solutions were mixed, by slightly tilting the flask, and shaken vigorously; after about two hours, the volume of the gas evolved was read with the usual precautions, and corrections for change of temperature and pressure during the period were applied. The quantity of the enolic form was calculated from the amount of methane evolved in the reaction. Occasionally a blank experiment was made to show that the dry *iso*amyl ether used as solvent did not develop any gas with the Grignard's reagent and to make sure that the ether did not absorb any moisture.

It has been recently shown by Hess and Rheinboldt[1] that magnesium methyl iodide yields ethane when treated with hydrochloric acid. Under the conditions mentioned in this paper, however the *iso*amyl-ethereal solution of hydrogen chloride did not give any gas with magnesium methyl iodide.

The results of these experiments are given in Tables I to V and shown graphically in the figure.

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[1] *Ber.*, 1921, 54, [*B*], 2043.

TABLE I.

Acetone and hydrogen chloride.

Gram of acetone	Amount of acid (%)	C.c. of gas at *N.T.P.*	Enolisation (%)
0·2904	1·21	10·51	9·4
0·1930	2·34	11·58	15·5
0·1066	4·08	8·65	21·0
0·0774	8·85	7·00	23·4
0·0282	13·74	4·60	42·3
0·0256	16·30	4·73	44·7
0·0240	20·40	4·84	52·2
0·0256	22·54	5·89	59·6
0·0240	29·90	6·96	75·1
0·0232	37·93	7·81	87·3
0·0248	50·06	9·23	96·4
Nil	0·0015 gram	Nil	Nil
0·3182	Nil	,,	,,

TABLE II.

Acetic acid and acetone.

Gram of acetone	Amount of acid	C.c. of gas at *N.T.P.*	C.c. of gas due to acid	Enolisation
Nil	0·0606 gram	24·56	...	Nil
0·1380	31·15%	17·45	17·79	,,
0·2020	21·09%	17·31	17·47	,,

TABLE III.

iso*Valeraldehyde and hydrogen chloride.*

Gram of aldehyde	Grams of acid	C.c. of gas at *N.T.P.*	Enolisation (%)
0·3446	Nil	7·34	8·2
Nil	0·0018	Nil	Nil
0·0592	1·13	,, [1]	15·8
0·0262	4·52	2·91	42·5
0·0264	6·61	3·41	49·5
0·0232	9·87	4·60	76·2
0·0222	10·47	4·71	81·5
0·0240	12·32	5·16	82·6
0·0246	12·55	5·58	87·1
0·0224	18·47	5 01	85·8

[1] Volume of gas due to acid = 2·44 c.c.

TABLE IV.

Propaldehyde and hydrogen Chloride.

Gram of aldehyde	Amount of acid (%)	C.c. of gas at *N.T.P.*	Enolisation (%)
0·2618	Nil	2·20	2·2
0·0288	8·79	2·02	18·1
0·0330	15·63	3·80	29·8
0·0378	17·01	5·27	36·1
0·0282	22·75	3·99	36·6
0·0248	32·52	6·24[1]	65·1
0·0276	38·44	8·23	76·7
0·0264	38·91	7·63	74·9
0·0482	46·56	9·30	79·2
0·0248	52·65	7·78	81·2

[1] A further 2 c.c. of gas were due to the acid.

TABLE V.

iso*Valeraldehyde and acetic acid.*

Gram of aldehyde	Gram of acid	C.c. of gas at *N.T.P.*	C.c. of gas due to acid	Enolisation Per cent.
Nil	0·0168	8·54	...	Nil
0·3812	0·0206	19·23	10·49	8·8
0·1946	0·0224	12·41	8·36	8·0

In all these experiments the vapour pressure of the amyl ether was neglected.

Summary and Conclusions.

The action of Grignard's reagent upon acetone, *iso*valeraldehyde, and propaldehyde in amyl-ethereal solution and in presence of acetic acid and of hydrogen chloride has been investigated with the following results :

(i) Acetic acid has no effect on the enolising action of Grignard's reagent, owing to decomposition immediately consequent on its exposure to the attack of the organo-metallic iodide. Lapworth (*loc, cit.*) ascribes the inability of acetic acid and similar acids to accelerate the halogenation of ketones (according to his theory by enolising them) to their weakly acid character.

(ii) Hydrogen chloride exerts a great influence on the enolisation of these aldehydes and acetone, the degree of enolisation being proportional to the quantity of acid present.

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