

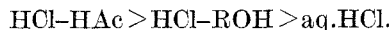
# THE HYDROLYSIS OF ACETONE-2,4-DINITROPHENYLHYDRAZONE\*

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As it is frequently necessary to recover a carbonyl compound from the hydrazone (for instance, after chromatographic separation of a mixture), the hydrolysis of acetone-2,4-dinitrophenylhydrazone was examined with a view to establishing conditions under which side reactions would be suppressed and a high yield of the ketone obtained.

Dicarbonyl compounds have been shown to be effective in regenerating aldehydes and ketones from their hydrazones by double decomposition (Strain 1935) and pyruvic acid, particularly, was examined by Fischer and Ach (1889).

Johnson and Stieglitz (1934) have shown that, in the hydrolysis of benzophenonehydrazone with either hydrochloric acid and acetic acid or with hydrochloric acid and a lower monohydric alcohol, the relative efficiency in preventing the formation of a ketazine is as follows :



When acetone-2,4-dinitrophenylhydrazone was hydrolysed with these solutions analogous results were obtained (Table 1).

TABLE 1

Reaction Mixture	Time of Refluxing before Distillation (hr.)	Acetone Reformed (Corrected) (%)
1.07N HCl (250 ml.)		
with glacial acetic acid (250 ml.) ..	2	68.5
" " " " " " ..	5.5	59.5
with propanol (250 ml.) .. ..	2	56.5
with water (250 ml.) .. ..	2	52.3
" " " " " " ..	4	41.0

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Inorganic buffer solutions were examined and it was found that a maximum rate of acetone regeneration occurred at pH 2, the acetone liberated amounting to some 94 per cent. 2N Hydrochloric acid and the constant boiling solution of the acid were also examined. The rôle of hydrochloric acid may be explained by a mechanism similar to that proposed by Johnson and Stieglitz (1934). It may be concluded, from the data in Table 2, that a high yield (94 per cent.) of acetone from its 2,4-dinitrophenylhydrazone is obtained by heating the hydrazone with (a) an aqueous solution containing a slight excess of pyruvic acid, or (b) an aqueous solution of an acid having pH 2.

### Experimental

Acetone-2,4-dinitrophenylhydrazone was prepared by the method of Iddles and Jackson (1934) in 96% yield, m.p. 126.5 °C.

In determining the efficiency of hydrolysis in the experiments the liberated acetone was distilled, from the reaction mixture in a 1 l. flask (in some cases after refluxing for a time), into an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2N hydrochloric acid. The resulting hydrazone was collected on a sintered glass crucible (2G4), washed, and dried to constant weight in a vacuum desiccator. Control experiments in which acetone was distilled from hydrochloric acid solution indicated that a correction factor of +3.6% was necessary to give quantitative recovery. The results (Table 1) support the previous observations of Johnson and Stieglitz (1934). In each experiment 0.8 g. of acetone-2,4-dinitrophenylhydrazone was used.

TABLE 2

No.	pH	Acetone Reformed (Corrected) (%)	Remarks
1	8.0	7.9	Acetone distilled off for 1 hr. " " " for a further hr. Distillation continued (5 hr.) until no more acetone distilled over
2	6.9	26.8	
3	6.9	28.0	
4	6.9	86.2	
5	5.2	42.4	2N HCl for reaction mixture Constant boiling HCl for reaction mixture A slight excess of pyruvic acid plus water to bring total volume to 500 ml. c. N/10 NaOH solution
6	3.2	84.7	
7	2.0	93.6	
8	1.4	92.8	
9	0.9	78.2	
10	Neg.	83.9	
11	Neg.	86.3	
12	—	93.9	
13	13	69.5	

Several hydrolyses were carried out using buffered solutions (made up from primary and secondary phosphates and hydrochloric acid), the pH's of which were checked with a quinhydrone electrode. Acetone was distilled for 1 hr. (except in Nos. 3 and 4) from the reaction mixture without prior refluxing, the volume being maintained at 500 ml. by the addition of water, or constant boiling hydrochloric acid in one case (No. 11). The m.p. of the reformed acetone-2,4-dinitrophenylhydrazone was within the limits  $126.5 \pm 0.5$  °C. In one case (No. 13) a white crystalline substance, having m.p. 90 °C., separated in the condenser and was probably *m*-dinitro-

benzene (Macbeth and Price 1937). In each experiment 1.0 g. of acetone-2,4-dinitrophenyl-hydrazone was used, and the results are recorded in Table 2.

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### References

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