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THE REACTION OF HYDROXYLAMINE HYDROCHLORIDE WITH α,β ETHYLENIC KETONES

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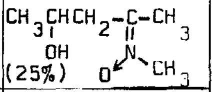
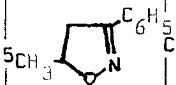
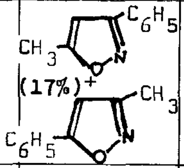
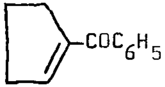
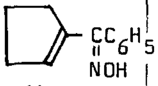
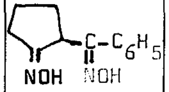
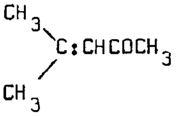
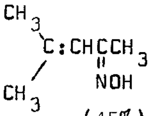
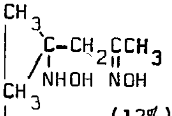
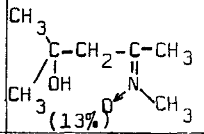
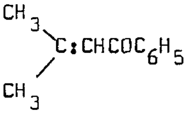
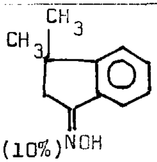
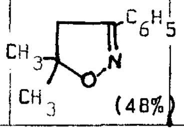
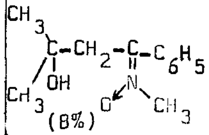
Until now only a restricted number of papers have dealt with the oximation of α,β ethylenic ketones. However it is not always easy to prepare the oximes of these ketones as the ethylenic bond can also react with hydroxylamine. This had been observed by Casey and Marvel[1] where the only isolated compounds are β-hydroxyl amino ketones. In the same way isoxazolines, which are most frequently encountered side products in the oximation of ethylenic ketones, results from an attack on both the ethylenic bond and on the carbonyl[2]. Because of these side reactions, some special methods have been developed to obtain ethylenic oximes. As the attack on the ethylenic bond decreases with the pH, it has been proposed that the oximation be carried out in acidic medium instead of the generally used alkaline medium[3]. Still more drastic is the method by Scott and al[4] in which hydroxylamine is reacted on a ketone where the ethylenic bond is blocked as a Mannich base; the ethylenic bond being regenerated once the oxime is made.

We have studied the reaction of hydroxylamine with ethylenic methyl ketones and with ethylenic phenyl ketones. Our results point out the high reactivity of the ethylenic bond. It is possible to isolate (case 2 and 4 table) a β-hydroxylamino oxime which results from a simultaneous attack on the ethylenic bond and on the carbonyl to give an important intermediate in the oximation reaction which has never been observed before. In the following table the studied ketones are presented as well as the isolated compounds and it can be observed that beside the oxime I and the isoxazoline II which are the expected compounds, there are five other types of products which had never been observed before in an oximation reaction: III, IV, V, VI and VII.

N°	KETONE	I	II	III	IV	V	VI	VII
1	$CH_3CH:CHCOCH_3$	$CH_3CH:CH\underset{NOH}{\underset{\|}{C}}CH_3$ (65%)			$CH_3\underset{NOH}{\underset{\|}{C}}CH_3$ (10%)			 (25%)
2	$CH_3CH:CHCOC_6H_5$	$CH_3CH:CH\underset{NOH}{\underset{\|}{C}}C_6H_5$ (2%)	 (53%)	$CH_3\underset{NHOH}{\underset{\|}{C}H}CH_2\underset{NOH}{\underset{\|}{C}}C_6H_5$ (10%)	$CH_3\underset{NOH}{\underset{\|}{C}}C_6H_5$ (18%)		 (17%)+	
3		 (70%)			$CH_3\underset{NOH}{\underset{\|}{C}}C_6H_5$ (10%)		 (20%)	
4		 (45%)		 (12%)	$CH_3\underset{NOH}{\underset{\|}{C}}CH_3$ (10%)	$CH_2:\overset{CH_3}{\overset{\vert}{C}}CH_2\underset{NOH}{\underset{\|}{C}}CH_3$ (20%)		 (13%)
5		 (10%)	 (48%)		$CH_3\underset{NOH}{\underset{\|}{C}}C_6H_5$ (12%)	$CH_2:\overset{CH_3}{\overset{\vert}{C}}CH_2\underset{NOH}{\underset{\|}{C}}C_6H_5$ (22%)		 (8%)

TABLE

The yields given refer to reactions carried out at room temperature in a basic medium,(methanol or water with sodium carbonate or sodium hydroxyde) with a ratio of hydroxylamine/ketone : 2/1. If the reaction is carried out at a different pH, the relative amounts of the products change. Particularly in the case of the three first compounds where the amount of one of those three compounds increases at the expense of the two others. For mesityl oxide for example, at neutral pH gives 30% oxime and 50% β-hydroxylamino oxime, whereas propenyl phenyl ketone, the amount of β-hydroxylamino oxime increases from 10% to 40%. The methyl ketones give the ethylenic oximes with a reasonable yield, whilst the phenyl ketones give very little oxime but more isoxazoline. With the exception of phenyl vinyl oxime[5]; all the ethylenic phenyl oximes obtained until now have an aryl ring β to the carbonyl group[1,3,6]. The β-hydroxylamino oxime is isolated mostly with neutral or slightly acidic media, whereas in alkaline medium isoxazolines and oximes are formed.

The saturated oxime (column IV) is isolated in all cases. Acetoxime is obtained when the starting compound is a methyl ketone and acetophenone oxime is obtained when the starting compound is a phenyl ketone. A somewhat similar cleavage has been observed recently with eneamines[7]. The non conjugated ethylenic oximes (column V) are obtained only when the β-carbon bears two substituents, but if the β carbon has a single substituent, oxidised compounds are obtained (column VI) (the dioxime is the oxidised form of the β-hydroxylamino oxime III, the isoxazole is the oxidised form of isoxazoline II). Two isomere isoxazoles are isolated, which suggests that their precursor is a dioxime. Such an oxidation in the course of an oximation is very remarkable as the products involved mainly show reducing properties[8,9].

Mechanistic studies are in progress to explain the formation of those products.

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