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A THERMAL REARRANGEMENT OF N-SUBSTITUTED BENZHYDROXAMIC ACIDS

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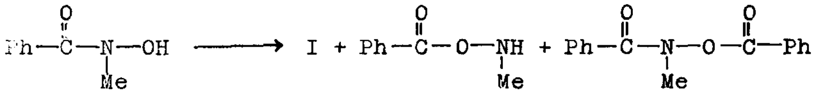
Hydroxamic acids are known to disproportionate on gentle heating (1) and at higher temperature decompose via a Lossen rearrangement (2). We wish to report a new rearrangement of N-substituted benzhydroxamic acids into the O-acylated isomers. As part of a series of investigations into the high nucleophilic reactivity of hydroxamic acids and related compounds we have prepared and attempted to purify by distillation, N-methylbenzhydroxamic acid (I). The distillate (b.p. 125° - 145°/0.3 mm.) was a mixture of unchanged acid and O-benzoyl-N-methylhydroxylamine, (II). The residue was O,N-dibenzoyl-N-methylhydroxylamine, (III), containing variable amounts of (I) and (II), depending on the distillation time.



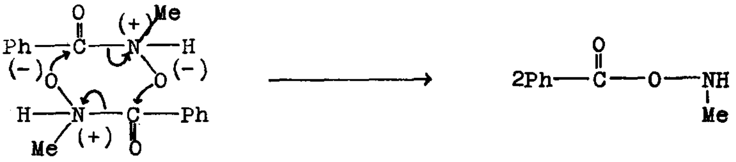
$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}\underset{Me}{N}{-}OH} \longrightarrow \mathrm{I} + \mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{Me}{NH}} + \mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}\underset{Me}{N}{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ph}$$

I II III

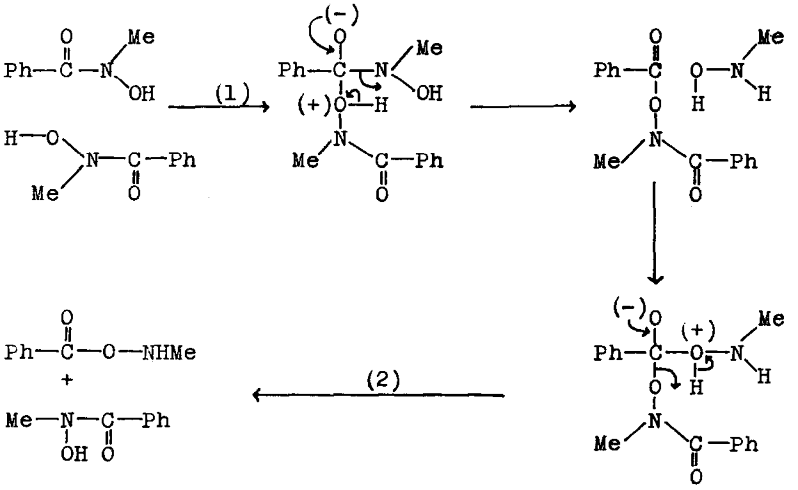
The isomers I and II could be separated by treatment with cold dilute aqueous alkali, the rearranged product remaining in the non-aqueous phase. O-Acylhydroxylamines and their N-alkyl derivatives have been prepared previously (3,4,5), by the acylation of the appropriate hydroxylamine, but often rapidly revert to the corresponding hydroxamic acid at room temperature. The O-aroyl-N-methylhydroxylamines reported in this communication are comparatively stable. At room temperature, those in the form of oils revert to the hydroxamic acids over a period of several weeks, while those in solid form are even more stable. All are stable in dilute solution (chloroform, petroleum ether) for several weeks, and may be distilled unchanged. It is this stability together with the inability of N-alkyl hydroxamic acids to undergo the Lossen rearrangement, which accounts for the present rearrangement.

The results of some typical distillations are shown in the Table. The components of distilled and residue were estimated by quantitative infra-red analysis. The solids did not rearrange on sublimation, but at increased pressures, rearrangement did occur in the molten phase. In view of the different temperatures which had to be employed for the various compounds, no conclusionscan be drawn at the present time on the influence of substituents on the course of the rearrangement.

The relative proportions of I and II were found to vary slightly with the length of the distillation, but the amounts of rearranged product never exceeded the amount of unchanged acid on a single distillation. These observations disfavour a mechanism which would produce O-aroyl-N-methylhydroxylamine only, e.g.



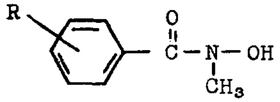
Moreover, such a mechanism gives no role for the O-N-diaroylhydroxylamine which comprises a large part of the residue. For these reasons we propose the following alternative mechanism,



According to such a mechanism the weight loss during distillation, calculated on the basis of N-methylhydroxylamine, should be equivalent to the amount of III produced. We find that N-methylhydroxylamine reacts with O,N-dibenzoyl-N-methylhydroxylamine to give both the acid I and the O-acyl compound II, as required by stage (2) of the above scheme.

Thermal rearrangement of N-methylbenzhydroxamic acids

(100 mmoles)



R	Conditions of distillation	Distillate (mmoles)		Residue (mmoles)			Wt.loss*
		I	II	I	II	III	
p-NO_2	185-200°/15mm.	8	7	27	14	18	26
H	125-145°/0.3mm.	52	16	13	2	7	10
p-MeO	135-150°/0.5mm.	29	27	21	4	7	12
p-Me	140-150°/15mm.	27	19	20	-	11	23
o-Me	155-185°/15mm.	57	27	-	-	12	4
2,4,6-tri Me	170-185°/15mm.	99	1	-	-	-	v. small 0

*Calculated as mmoles of $NH(CH_3)OH$

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