ACID HYDROLYSIS OF 2-IMINOPERHYDROTHIENO[3,4-d]-OXAZOL-5,5-DIOXIDES

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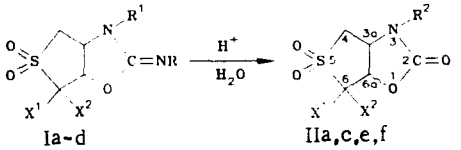
We have found that refluxing 2-iminooxazolidines Ia-c for 5-15 min in aqueous acetic acid readily causes hydrolytic cleavage of the C=N bond and formation of the 2-oxazolidines IIa,c (R^2 = $COCH_3$) in 75-80% yield. Under the same conditions using hydrochloric acid the C=N bond is cleaved only in the cis-oxazolidines Ic, d, moreover the 3-acetyl group is simultaneously cleaved to form the oxazolidones IIe, f (R^2 = H, yield up to 70%).



Ia-d IIa,c,e,f

I a, b *trans*- $X^1=X^2=H$, $R^1=COCH_3$; a $R=C_6H_5$, b $R=CH_2C_6H_5$; I c, d *cis*- $R=R^1=COCH_3$; c $X^1=X^2=Br$; d $X^1=Br$, $X^2=H$; II a *trans*- $X^1=X^2=H$, $R^2=COCH_3$; II c,e, f *cis*- $X^1=Br$; c $X^2=Br$, $R^2=COCH_3$; e $X^2=Br$, $R^2=H$; f $X^2=R^2=H$

Under the influence of hydrochloric acid the trans-oriented oxazolidines Ia, b also readily lose the CH_3CO group but preserve the C=NR fragment unchanged. The trans-oriented iminooxazolidines not substituted in the 3-position are stable under the acid hydrolysis conditions.

The elemental analytical data for S, N, and Br in the oxazolidones II agreed with that calculated. In their IR spectra the absorption at 1760-1800 cm^{-1} was typical of the carbonyl group in a five membered ring. The PMR spectra (in DMSO-d_6) showed the absence of protons for the R substituents. The remaining proton signals in the order given (in ppm relative to TMS) were: CH_3, 3α-H, 6α-H, 4-H, 4'-H, 6-H, 6'-H, NH: IIa, 2.39, 5.02, 5.33, 3.33, 3.49, 3.51, 3.60, —; IIc 2.39, 5.22, 5.60, 3.92, 4.12, —, —, —; IIe —, 4.80, 5.61, 3.56, 3.90, —, —, 8.41; IIf —, 4.69, 5.37, 3.38, 3.72, 5.79, —, 8.16.

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