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CURTIUS REARRANGEMENT OF 1(2H)-ISOQUINOLINE- AND 1H-2-BENZOPYRAN-1-ONE CARBOXYLIC ACIDS

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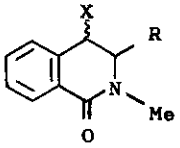
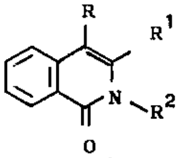
Within a programm of synthesis of isoquinoline- and 1-2H-benzopyran derivatives the reactivity of the isomeric acids trans- and cis-1a, 2a-5a and 6a,7a is studied systematically under the Curtius reaction conditions. It is found that 1a-4a, 6a and 7a are easily transformed into amines (carboxamides resp.) or carbamates. By means of ^{1}H-NMR-analysis it is proved that the conversion of the diastereomeric 1a proceeds stereospecifically. The attempts for the preparation of the azides of 4a and 5a[1] via the corresponding acid chlorides or anhydrides show that the acylating reagents ($SOCl_2$, $ClCO_2Me$ and others) attack the lactam rather than the carboxylic function.

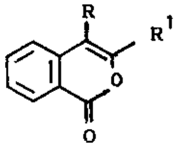
The structure and the reactivity of the acids 2a-7a are discussed on the basis of the ^{13}C-NMR-spectra of the parent compounds and some of their derivatives.



trans-1a-h; cis-1a-d
R =Ph or $C_6H_3(MeO)_2$-3,4



2a-g : R = X, R^1= H, R^2= Me
3a-d : R = X, R^1= R^2= H
4a,e : R = H, R^1= X, R^2= Me
5a : R = R^1= H, R^2= H



6a-d, 6h : R = X, R^1= H
7a-d, 7h : R = H, R^1= X

X : a = CO_2H, b = COCl, c = CON_3
d = $NHCO_2Me$, e = $NHCO_2CH_2Ph$
f = NH_2, g = $NHCOCH_2Ph$
h = NHCOMe

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1. T. Hashimoto, S. Nagase, Yakugaku Zasshi, 80, 1806 (1960); C.A.55, 9400h