

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

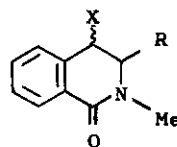
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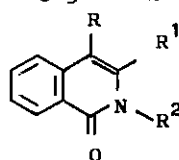
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Within a programm of synthesis of iso- 1. T. Hashimoto, S. Nagase, Yakugaku
quinoline- and 1-2H-benzopyran deriva- Zasshi, 80, 1806 (1960); C.A.55, 9400h
tives the reactivity of the isomeric
acids trans- and cis-1a, 2a-5a and 6a,7a
is studied systematically under the Cur-
tius reaction conditions. It is found
that 1a-4a, 6a and 7a are easily trans-
formed into amines (carboxamides resp.)
or carbamates. By means of ¹H-NMR-ana-
lysis it is proved that the conversion
of the diastereomeric 1a proceeds stereo-
specifically. The attempts for the pre-
paration of the azides of 4a and 5a¹ via
the corresponding acid chlorides or an-
hydrides show that the acylating rea-
gents (SOCl₂, ClCO₂Me and others) attack
the lactam rather than the carboxylic
function.

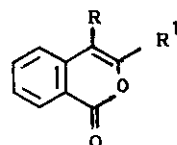
The structure and the reactivity of
the acids 2a-7a are discussed on the ba-
sis of the ¹³C-NMR-spectra of the parent
compounds and some of their derivatives.



trans-1a-h; cis-1a-d
R = Ph or C₆H₃(MeO)_{2-3,4}



2a-g : R = X, R¹ = H, R² = Me
3a-d : R = X, R¹ = R² = H
4a,e : R = H, R¹ = X, R² = Me
5a : R = R¹ = H, R² = H



6a-d, 7h : R = X, R¹ = H
7a-d, 7h : R = H, R¹ = X

X : a = CO₂H, b = COCl, c = CON₃
d = NHCO₂Me, e = NHCO₂CH₂Ph
f = NH₂, g = NHCOCH₂Ph
h = NHCOMe