HETEROCYCLES, Vol. 4, No. 10, 1976

AN INTRAMOLECULAR REARRANGEMENT OF 1-ARYLAZETIDIN-2-ONES IN AN ACIDIC SOLUTION

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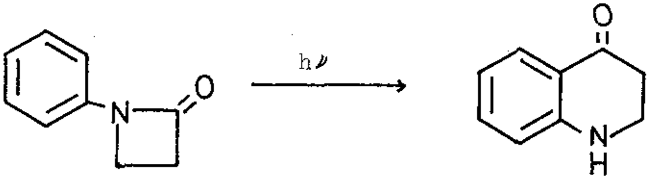
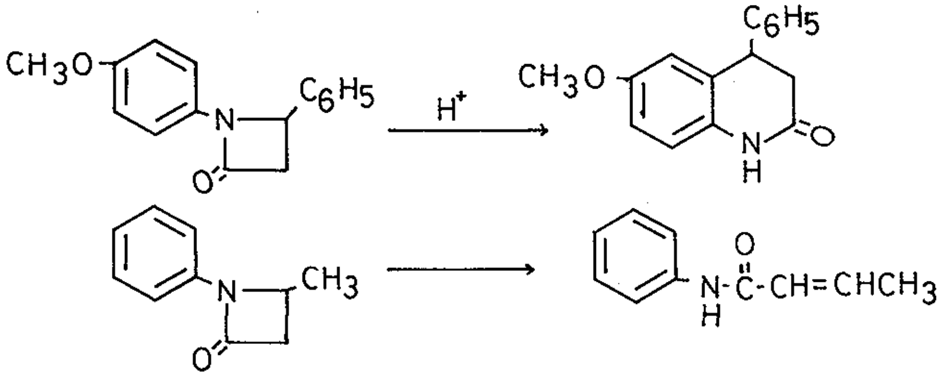
Several kinds of 1-arylazetidin-2-ones were treated with trifluoroacetic acid to give 1,2,3,4-tetrahydroquinolin-4-ones. In the case of 1-arylazetidin-2-ones possessing a substituent at the 3-position, the rearrangement occurred at both ortho- and para-positions to the substituent located at the 3-position.

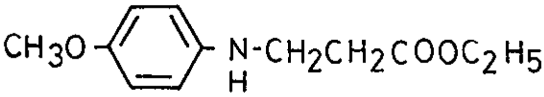
Several works have been reported a transformation of 1-arylazetidin-2-ones to 1,2,3,4-tetrahydroquinolin-4-one by photolysis[1], and to 3,4-dihydrocarbostyrils by the action of an acid[2]. Furthermore, 1-arylazetidin-2-ones have been known to undergo 1,4-heterolytic cleavage and subsequent prototropic shift to give the corresponding amides[3]. Thus 1-arylazetidin-2-ones have been proposed as a reactive intermediate for a synthesis of some N-heterocycles.





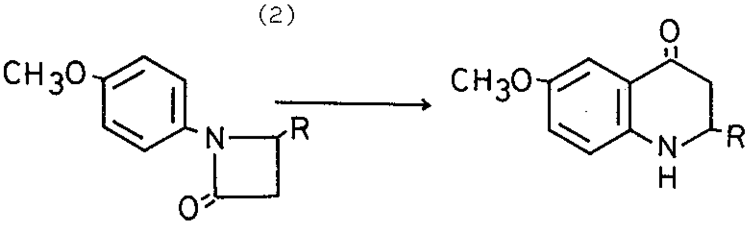
In this communication we wish to report a rearrangement of 1-arylazetidin-2-ones leading to formation of 1,2,3,4-tetrahydroquinolin-4-ones through a cleavage of the $N-C_2$ bond.

First, 1-(4-methoxyphenyl)azetidin-2-one (1), prepared through cyclization of ethyl β-(*p*-methoxyanilino)propionate (2) with ethylmagnesium bromide[4], was heated in trifluoroacetic acid to give 1,2,3,4-tetrahydro-6-methoxyquinolin-4-one (3), mp 112-113° (lit.[5], 113.5-114.5°) in quantitative yield. Similarly, the same treatment of 1-(4-methoxyphenyl)-4-methylazetidin-2-one (4), obtained by the same manner as in formation of (1), with trifluoroacetic acid afforded 1,2,3,4-tetrahydro-6-methoxy-2-methylquinolin-4-one (5), mp 139-140° (benzene-ether) [i.r.($CHCl_3$) 1650 cm^{-1}(C=O); nmr ($CDCl_3$) δ 1.32 (3H, d, *J*=6 Hz, 2-CH_3), 3.75 (3H, s, OCH_3), 6.59 (1H, d, *J*=9 Hz, 8-H), 6.96 (1H, d,d, *J*=3 and 8 Hz, 7-H), 7.28 (1H, d, *J*=3 Hz, 5-H); *m/e* 191 (M^+), 176, 161, 149, 133], quantitatively. When 1-(*m*-tolyl)azetidin-2-one (6) was treated with trifluoroacetic acid, both *ortho* and *para* rearrangements with reference to the methyl group at the 3-position proceeded smoothly, and 1,2,3,4-tetrahydro-7-methylquinolin-4-one (7) [30 %; mp 93-95 (methanol-ether); nmr ($CDCl_3$) δ 2.26 (3H, s, 7-CH_3),



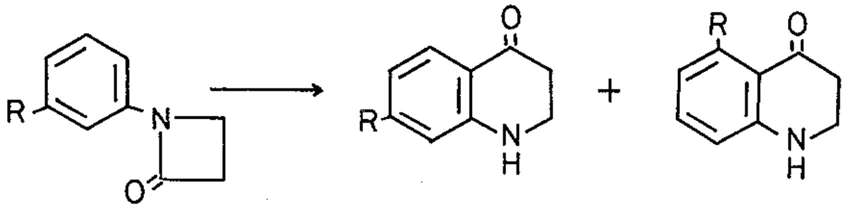
(2)

$CH_3O-C_6H_4-NH-CH_2CH_2COOC_2H_5$



(1) R=H
(4) R=CH_3

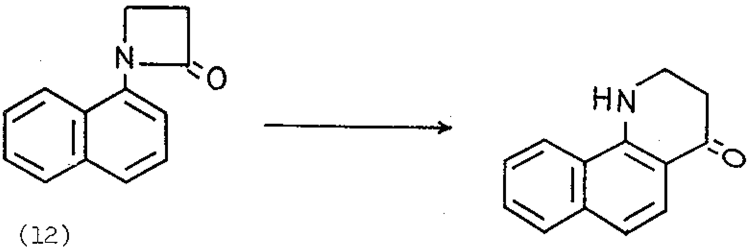
(3) R=H
(5) R=CH_3



(6) R=CH_3
(9) R=OCH_3

(7) R=CH_3
(10) R=OCH_3

(8) R=CH_3
(11) R=OCH_3



(12)

(13)

6.46 (1H, d, J=1 Hz, 8-H), 6.53 (1H, d,d, J=1 and 8 Hz, 6-H), 7.72 (1H, d, J=8 Hz, 5-H); m/e 161 (M^+), 146, 133] and 5-methyl isomer (8) [30 %; mp 97-98°(methanol-ether); nmr ($CDCl_3$) δ 2.59 (3H, s, 5-CH_3), 6.49 (2H, d,d, J=7 and 8 Hz, 6-H and 8-H)[6], 7.05 (1H, d,d, J=7 and 8 Hz, 7-H); m/e 161 (M^+), 146, 133] were isolated by silica gel column chromatography. Similarly, a rearrangement of carbonyl group of 1-(3-methoxyphenyl)azetidin-2-one (9) also occurred at both ortho and para positions with reference to the methoxy group to give two products which were separated by column chromatography on silica gel. The first product, yielded from benzene-chloroform (8:2) fraction in 40 % yield, was assigned to 7-methoxy-1,2,3,4-tetrahydroquinolin-4-one (10), mp 138-139°(methanol-ether), [nmr ($CDCl_3$) δ 3.77 (3H, s, OCH_3), 6.05 (1H, d, J=2.5 Hz, 8-H), 6.27 (1H, d,d, J=2.5 and 8.5 Hz, 6-H), 7.75 (1H, d, J=8.5 Hz, 5-H); m/e 177 (M^+), 149; i.r.($CHCl_3$) 1650 cm^{-1} (C=O)]. The second one, obtained from chloroform-methanol (98:2) fraction in 20 % yield, was determined as the 5-methoxy isomer (11), mp 183-184°(methanol-ether), [nmr ($CDCl_3$) δ 3.84 (3H, s, OCH_3), 6.18 (1H, d, J=8 Hz, 6-H or 8-H), 6.22 (1H, d, J=8 Hz, 6-H or 8-H), 7.15 (1H, t, J=8 Hz, 7-H); m/e 177 (M^+), 149; i.r.($CHCl_3$) 1650 cm^{-1}(C=O) .

Finally, an acidic rearrangement of 1-(α-naphthyl)azetidin-2-one (12) in trifluoroacetic acid was also examined to give the benz[h]-quinolin-4-one (13) in 40 % yield, mp 158-160°(methanol-ether), [nmr ($CDCl_3$) δ 7.08 (1H, d, J=9 Hz, 6-H), 7.86 (1H, d, J=9 Hz, 5-H), 7.30-7.88 (4H, m, other aromatic H); m/e 197 (M^+), 169, 141].

It is noteworthy that the different mode of rearrangement from the similar works in the literature[2] was observed.

ACKNOWLEDGEMENT

we thank Mr. Y. Shida, Mr. S. Suzuki, Miss C. Takagai for spectroscopic measurements. We wish to express our gratitude to Mr. S. Suzuki and Mr. H. Kitsunezaki for their technical assistance.

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6 The signals due to 6-H and 8-H were observed at the same position $J_{6,7}$=7 or 8 Hz, $J_{7,8}$=7 or 8 Hz

Received, 9th August, 1976