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CHALCONE OXIMES. PART VI *
NOVEL REARRANGEMENT OF 2,3-DIHYDRO-BENZO-γ-PYRONE OXIMES INTO Δ^2-ISOXAZOLINE DERIVATIVES

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Abstract - The (E) 2,3-dihydro-2-(R-phenyl)-4H-benzopyran-4-one oximes (1a - f) have been transformed into corresponding isomeric Δ^2-isoxazolines (2a - f) by treatment with trifluoroacetic acid.

Recently we have described the transformation of (E) 2,3-dihydro-2-(R-phenyl)-4H-benzopyran-4-one oximes into isomeric (E) 1-(2-hydroxyphenyl)-3-(R-phenyl)-2-propen-1-one oximes [1].

On the basis of ^1H NMR data, the (E) configuration was assigned for the starting compounds. The same configuration was also established for the reaction products on the basis of the results of Beckmann rearrangement leading in this case to the 2-styrylbenzoxazoles.

At present we wish to report the novel rearrangement of (E) 2,3-dihydro-2-(R-phenyl)-4-H-benzopyran-4-one oximes into isomeric Δ^2-isoxazoline derivatives. Thus, when (E) oximes (1a - f) [1] were treated with boiling trifluoroacetic acid (for 90 min.), the corresponding Δ^2-isoxazoline derivatives (2a - f) were obtained. The melting points, yields and the spectral data of the resulting Δ^2-isoxazolines as well as their acetyl derivatives are listed in Table 1. We assume that the reaction sequence should involve two steps as depicted in Scheme 1.

The use of well-known isomerizing agent i.e. trifluoroacetic acid [2] causes a hydrolytic ring-opening and recyclization of intermediate oxime to the Δ^2-isoxazoline derivative.

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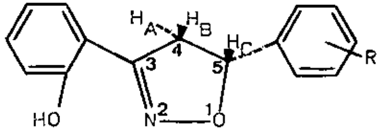
Properties and spectral data of Δ^2-isoxazolines (2a-2f) [x]



Com-pound	R	Yield %[a]	M.p. [x] °C	R_f [xx]	UV λ_{max}^{EtOH} nm (log ε)	IR ν_{max}^{KBr} (cm^{-1})		
						-C=N	-OH	$-CH_2$
2a	4-OH[b]	66	86-88	0.62	220, 265, 275, 308 (4.27 ,(4.11),(3.98),(3.77)	1615	3140	2900
2b	$4-OCH_3$[c]	70	78-80	0.81	222, 264, 274, 308 (4.30),(4.11),(4.00),(3.76)	1610	3120	2900
2c	$4-OCH_2CH_3$	75	83-85	0.75	225, 265, 275, 306 (4.32),(4.05),(3.96),(3.77)	1600	3200	2940
2d	$3,4-OCH_3$[c]	83	116-118	0.68	217, 265, 274, 308 (4.32),(4.10),(4.03),(3.80)	1615	3080	2920
2e	$3,4,5-OCH_3$	80	135-137	0.65	220, 264, 273, 307 (4.26),(4.12),(3.99),(3.75)	1590	3140	2920
2f	$3,4-OCH_2O-$[c]	66	94-96	0.84	218, 265, 274, 288, 308 (4.20),(4.15),(4.05),(4.09),(3.87)	1610	3140	2890

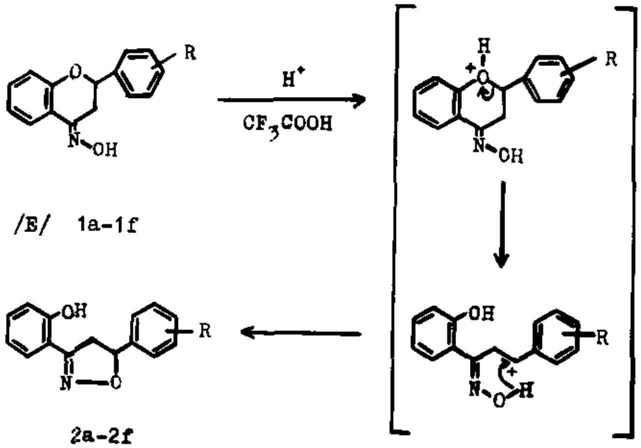
Table 1 (continued)

Compound	^1H NMR δ in ppm [xxx]							Acetyl derivative	
	-OH	$-H_A$ $-H_B$	$-H_C$	J_{AB} (Hz)	J_{BC} (Hz)	J_{AC} (Hz)	$-OCH_3$	M.p. °C [x]	IR ν_{max}^{KBr} (cm^{-1}) $-COCH_3$
2a	7.96(s) 9.85(s)	3.16(dd) 3.63(dd)	5.46(t)	17	11	8.5	-	102-104	1755
2b	9.8 (s)	3.21(dd) 3.73(dd)	5.33(t)	17	11	8	3.83(s)	122-124	1740
2c	9.8 (s)	3.26(dd) 3.73(dd)	5.4 (t)	17	12	8	1.26(t)	147-149	1755
2d	9.76(s)	3.1 (dd) 3.76(dd)	5.4 (t)	17	11	8	3.81(s) 3.83(s)	96-98	1760
2e	9.73(s)	3.1 (dd) 3.7 (dd)	5.4 (t)	17	12	8	3.80(s) 3.83(s)	108-109	1750
2f	9.73(s)	3.1 (dd) 3.56(dd)	5.36(t)	17	12	9	5.93(s)	oil	1755

x All compounds gave satisfactory elemental analyses. Melting points are uncorrected.

xx TLC Kieselgel $60F_{254}$, benzene-ethyl acetate 38:12 (V/V). xxx ^1H NMR spectra were recorded on a VARIAN EM-360 (60 MHz) spectrometer in $CDCl_3$ solution. a/ All compounds were recrystallized from ethanol, only **2a** were recrystallized from n-hexane. b/ (Z)→(E) isomerization of starting oxime under reaction conditions was observed. c/ The starting oximes was previously reported by C.O'Brien et.al. Tetrahedron, 1963, **19**, 373.

The oximes with the following substituents 4'-Cl, 4'-Br, 4'-J, $4'-CH_3$ and $4'-NO_2$ were not rearranged under above mentioned reaction conditions.



Scheme 1

The formation of oxime is supported by known lability of the 2,3-dihydro-benzo-γ-pyrones especially towards bases [1,3-5].

The hydrolytic ring-opening of 2,3-dihydro-2-phenyl-4H-benzopyran-4-one oxime leading to 3-(2-hydroxyphenyl)-5-phenyl- Δ^2-isoxazoline was reported in 1961 by Venturella and Bellino [4]. In a succesive paper [5] however the authors revised the structure of the product and claimed it to be 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one oxime. In the light of this revision, the present work describes the first rearrangement of oximes of 2,3-dihydro-benzo-γ-pyrones into Δ^2-isoxazoline derivatives.

The observation of the formation of Δ^2-isoxazoline derivatives prompted us to investigate the TFA catalysed rearrangement of isomeric 1-(2-hydroxyphenyl)-3-(R-phenyl)-2-propen-1-one oximes [1]. The results will be published separately.

After completion of this work a very similar rearrangement of oximes of dihydropyronic derivatives into Δ^2-isoxazoline was recently reported by Payard et.al. [6].

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