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NOVEL REACTIONS OF CARBON SUBOXIDE. IV. SYNTHESIS OF SOME N-HYDROXY-2-OXO-2H-1-BENZOPYRAN-3-CARBOXAMIDES

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Summary: Some N-hydroxy-2-oxo-2H-1-benzopyran-3-carboxamides have been prepared by reaction of carbon suboxide with 2-hydroxyaryloximes.

As a part of investigations on the use of carbon suboxide in the synthesis of new heterocyclic compounds with potential biological activity[1,2], we describe in this paper the synthesis of several N-hydroxy-2-oxo-2H-1-benzopyran-3-carboxamides (3a-f), in one only step, starting from 2-hydroxyaryloximes (1a-f) (Scheme 1).

They are possibly formed through rapid rearrangement reactions of the derivatives which are obtained in a first step of the reaction of direct cycloaddition of carbon suboxide to 2-hydroxyaryloximes[3].

The carboxamides (3a-f) are converted into the respective carboxylic acids (4a-f)[4,8] by hydrolysis. The results are presented in the Tables 1 and 2.

The structure of derivatives (3) was determined by analytical and spectroscopic data. In fact, they show a characteristic OH band between 3400 and 3200 cm^{-1}, δ-lactonic C=O bands and bands of extranuclear amidic C=O, bonded in position 3 as from δ-lactonic cycle, between 1820 and 1640 cm^{-1} [9]; ^{1}H-NMR spectra show a NH amidic signal between about δ 9 and δ 11, a signal between about δ 8.1 and δ

8.9 attributed to proton 4 and, moreover, the aromatic protons and the hydroxyl group signals. Finally, mass spectra, besides the molecular ion, show the base peak at (M^+-NHOH) and the peak at (M^+-CONHOH).

Table 1

Preparation of compounds 3

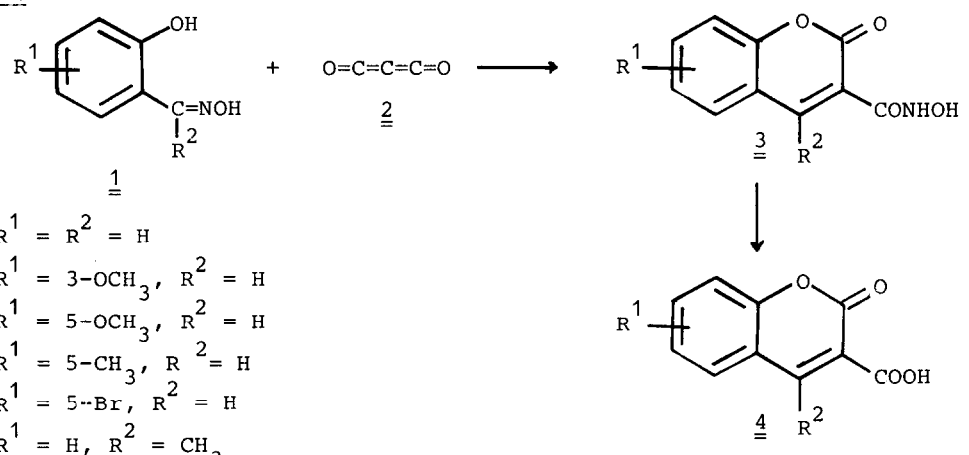
Compound No	Molecular formula[a]	Yield (%)[b]	M.p. (°C)	I.R. (nujol) cm^{-1} ν(O-H)	ν(C=O)	Mass data (m/e)
3a	$C_{10}H_7NO_4$	70	207	3300	1770, 1720, 1640	205 (M^+), 173, 145
3b	$C_{11}H_9NO_5$	80	121	3400	1820, 1780, 1760	235 (M^+), 203, 175
3c	$C_{11}H_9NO_5$	76	110	3400	1820, 1800, 1780, 1760, 1650	235 (M^+), 203, 175
3d	$C_{11}H_9NO_4$	69	135	3440	1770, 1760, 1730, 1700	219 (M^+), 187, 159
3e	$C_{10}H_6BrNO_4$	88	136	3200	1790, 1770, 1730, 1700	283-285 (M^+), 251-253, 223-225
3f	$C_{11}H_9NO_4$	67	120	3420	1790, 1760, 1720	219 (M^+), 187, 159

a) All products gave satisfactory elemental analyses; b) isolated yield of pure material.

Representative Experimental Procedure: To a stirred solution of 2-hydroxyarylo-xime (1) (0.016 moles) in dry diethyl ether (250 ml), carbon suboxide (2) (0.016 moles) was added during 2 hours at -70°C. When the addition was complete, the mixture was stirred at 0°C for 4 hours and then allowed to warm and left at room temperature for 3 days with stirring. The precipitate was filtered and crystallized from ethanol to give (3) as tablet shaped yellow crystals.

These products, after hydrolysis with 20% aqueous sodium hydroxide, furnished the acids (4).

SCHEME 1



1

1a $R^1 = R^2 = H$
1b $R^1 = 3\text{-}OCH_3$, $R^2 = H$
1c $R^1 = 5\text{-}OCH_3$, $R^2 = H$
1d $R^1 = 5\text{-}CH_3$, $R^2 = H$
1e $R^1 = 5\text{-}Br$, $R^2 = H$
1f $R^1 = H$, $R^2 = CH_3$

3a, 4a $R^1 = R^2 = H$
3b, 4b $R^1 = 8\text{-}OCH_3$, $R^2 = H$
3c, 4c $R^1 = 6\text{-}OCH_3$, $R^2 = H$
3d, 4d $R^1 = 6\text{-}CH_3$, $R^2 = H$
3e, 4e $R^1 = 6\text{-}Br$, $R^2 = H$
3f, 4f $R^1 = H$, $R^2 = CH_3$

Table 2

80 MHz-^{1}H-NMR spectral data of compounds 3, δ ppm[a]

Compound No	R^1	R^2	Ar-H	OH	NH
3a		8.92 (s, 1H)	8.05-6.86 (m, 4H)	10.79 (s)	10.36 (s)
3b	3.80 (s, 3H)	8.15 (s, 1H)	7.42-6.58 (m, 3H)	9.12 (s)	9.80 (s)
3c	3.75 (s, 3H)	8.36 (s, 1H)	7.18-6.63 (m, 3H)	9.00 (s)	9.11 (s)
3d	3.75 (s, 3H)	8.64 (s, 1H)	7.36-6.80 (m, 3H)	5.11 (s)	9.48 (s)
3e		8.07 (s, 1H)	7.40-6.76 (m, 3H)	6.25 (s)	9.84 (s)
3f		3.63 (s, 3H)	7.63-6.80 (m, 4H)	4.16 (s)	10.98 (s)

a) 3a was measured in DMSO-d_6, 3b and 3c in $CDCl_3$, 3d, 3e and 3f in $(CD_3)_2CO$.

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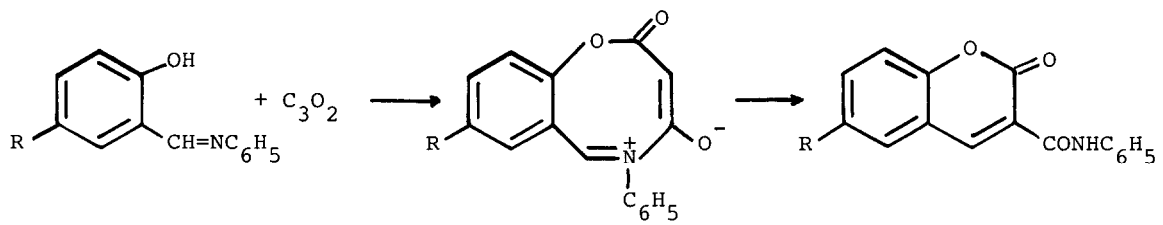
3. This is justified by the fact that during the re-examination of some reactions of carbon suboxide and azomethines[10,11] we have noticed the formation of mesoionic intermediates which are swiftly converted into coumarin-3-carboxamidic derivatives:



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8. 4c: mp 195-195.5°C; IR (nujol): 3360 (OH), 1740, 1670 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$), δ: 9.78 (s, 1H, OH), 8.13 (s, 1H, H-3), 7.32-6.60 (m, 3H, Ar-H), 3.72 (s, 3H, OCH_3); M^+ (m/e): 220.
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