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ORIGINAL PAPER

Hydroxylamine and Pseudoacyl Systems: Pseudo-oximes

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Abstract Unhindered furan pseudoacyl chlorides react with hydroxylamine and a carbonate base to form oxidized cyclic *N*-hydroxyiminoimides. Thus, 3-chloroisobenzofuran-1-one forms 3-hydroximinoisoindolin-1-one (**4**) $C_8H_6N_2O_2$. Molecules are nearly planar and *E*-secondary amides hydrogen-bond with oximes through N(H)···N 2.920 Å and O(H)···O 2.720 Å contacts, and form infinite chains. Mucochloryl chloride (2,3,4-trichlorodihydrofuran-1-one) forms a similar hydroxyiminoimide (5*E*)-3,4-dichloro-5-hydroxyiminopyrrol-2-one (**6**), $C_4H_2Cl_2N_2O_2$. However, opianic acid forms a mixture of mostly *N*-hydroxyphthalimide [6,7-dimethoxy-*N*-hydroxyisoindolin-1,3-dione (**9**)], $C_{10}H_{10}N_2O_2$, with small amounts of open oxime carboxylate [potassium 2,3-dimethoxy-6-(*N*-hydroxymethanoyl)benzoate (**8**) $C_{10}H_{10}NO_5K$], and 2,3-dimethoxyphthalimide (**10**), $C_{10}H_9NO_4$. These results suggest an intermediate pseudo-oxime, and such a derivative has been made in quantitative yield in a dehydration resistant arylpyran pseudoacyl system. 3-Chloro-4,4-dimethylisobenzopyran-1-one reacts with two equivalents of hydroxylamine and a carbonate base to form 2-hydroxy-3-(hydroxyamino)-4,4-dimethyl-3H-isoquinolin-1-one (**14**), $C_{11}H_{13}N_2O_3$, a pseudo-oxime. Pairs of pseudo-oximes form four hydrogen-bonds in two complementary sets, with N(H)···O 3.008 Å and O(H)···O 2.685 Å. Molecules are also linked in chains by hydrogen-bonds with O(H)···O 2.696 Å. These products have been characterized by spectroscopy and X-ray diffraction.

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Introduction

Pseudoacids are cyclic oxocarboxylic acids, typically formed by intramolecular interaction of an aldehyde/ketone with a carboxylic acid function [1]. The open-cyclic equilibrium favors the cyclic structures where the interacting groups are brought closer together such as in *cis*-alkenes and *o*-disubstituted aryl systems [2, 3]. Pseudoacids form a range of modified acid derivatives which are analogous to yet distinct from those of normal carboxylic acids, such as pseudoacyl halides, pseudoesters, pseudoamides and pseudoanhydrides [4]. But pseudoacids are also pseudo-aldehydes/ketones. Reaction outcomes produce typical carbonyl derivatives in strained systems such as *o*-benzoylbenzoic acid [5] or cyclic structures (substituted furanones, pyridazones) in other systems [6]. For the oxime, pseudoacid systems have been reported to form open-chain oxime/carboxylates with a strong base and hydroxylamine [7]. Levulinic acid is an aliphatic γ-oxocarboxylic acid with an open-cyclic equilibrium that favors the open form over the furanoic pseudoacid. It produces an open oxime/acid when treated with hydroxylamine and a base [8]. There is a liability toward oxidation in some furanoid pseudoacid systems such as opianic acid to hemipinic acid [9]. Use of hydroxylamine to form cyclic imides from cyclic anhydrides has recently been reported [10], which suggests that the products of pseudoacids and hydroxylamines also should be examined carefully. Nitrogen derivatives of arylpyran pseudoacids have not been pursued to any great degree, so an initial comparison between the furanoid and pyranoid systems might prove interesting. Since oxime derivatives give rise to modified spectral properties with somewhat

equivocal interpretations, crystallographic means were also employed to identify the phases produced. In this work, we report the results of the reactions of hydroxylamine with several pseudoacid systems in the presence of carbonate as the base and in polar protic and aprotic solvents.

Experimental

Reagents and solvents were obtained from Aldrich Chemical Corp., VWR Scientific, and TCI Chemical Corp. and used as received. 3-Chloroisobenzofuran-1-one (**1**) was made from *o*-formylbenzoic acid by a literature method [11]. Mucochloryl chloride (2,3,4-trichlorodihydrofuran-1-one, **2**) was made from mucochloric acid, and freshly distilled before use (bp 55 °C, 0.5 Torr). The pseudoacid 3-hydroxy-4,4-dimethylisobenzopyran-1-one (**3**) was made by a literature method [12].

3-Hydroximinoisoindolin-1-one (**4**)

To a solution of 0.050 g (0.30 mmol) **1** in 5.0 mL 95 % ethanol was added 0.208 g (3.0 mmol) hydroxylamine hydrochloride and 0.42 g (3.0 mmol) potassium carbonate. The mixture was stirred for 2 days at 25 °C during which the initially colorless mixture became yellow. Then, the solvents were evaporated under an air stream, and the residue suspended in 10 mL water, and filtered. The insoluble organic component was dissolved in ethanol, and allowed to slowly crystallize producing prisms, 0.049 g (19 %), mp 255.9–257.3 °C. Analysis: ^{1}H-nmr, CD_3OD, δ 7.6–8.0, multiplets, 4H, aryl-Hs; δ 4.8, s, 1H, N–H; δ 3.3, s, 1H,=N–OH; ^{13}C-nmr, $CDCl_3$; 120.3, 122.9, 130.2, 132.7, aryl C–Hs; 134.1, 145.5, aryl C; 168.0, C=O, 178 C=N–OH; IR (solid, cm^{-1}): 3424 (broad), νNH; 3215, νOH; 2953 (w), νCH aryl; 1706 9 (s), νC=O; 1678 (m), νC=N. Reaction conditions employing pyridine or triethylamine as base and solvent blackened and no identifiable products could be extracted.

(5*E*)-3,4-Dichloro-5-hydroxyiminopyrrol-2-one (**6**)

Mucochloryl chloride (**2**), 0.376 g (2.0 mmol) was dissolved in 2.5 mL 95 % ethanol and 0.690 g (9.9 mmol) hydroxylamine hydrochloride and 1.40 g (10.1 mmol) potassium carbonate were added. The mixture was stirred for 3.5 days at 25 °C, during which the initially colorless mixture became yellow. The solvent was evaporated in an air stream, and the residue treated with water and filtered; the insoluble organic phase was recrystallized from ethanol to produce colorless plates, 0.250 g (69 %) mp 155 °C. Analysis: ^{1}H-nmr CD_3OD, 25 °C δ 5.0, s, 1H, N–H; δ 4.5, s, 1H, –OH; ^{13}C-nmr, CD_3OD; δ 161.3, C=O, δ 143.6, 133.0,=C–Cl's; δ 84.1 C=N–OH; IR (solid, cm^{-1}): 3196, νNH/OH; 1709 (s), νC=O; 1688 (s), νC=N; ν1651 (m), νC=C; 1589 (w); 1550 (w); 1386 (w); 1329 (w); 1290 (m); 1240 (m); 1100 (s); 1059 (m); 965 (s) γ(alkene); 880 (m); 720 (s) νC–Cl.

N-Hydroxy-5,6-dimethylphthalimide (**10**)

Opianic acid is converted quantitatively to its pseudoacyl chloride (**7**) by treating with excess thionyl chloride. The colorless solid **7** is a moisture sensitive solid, analysis: ^{1}H-nmr: $CDCl_3$, 25 °C: δ 7.3, 2H, dd; 4.11, s, 3H, OMe; 3.96, s, 3H, OMe; ^{13}C-nmr: $CDCl_3$, 25 °C: δ164.9, C=O; 154.0, 148.1, Ar*C*–OMe; 139.7, 119.7, 118.3, 116.2, ArC's; 85.1, C–Cl; 62.4, 56.8, OCH_3s. Opianyl chloride (**7**), 0.109 g (0.48 mmol) is combined with 0.33 g (4.8 mmol) hydroxylamine hydrochloride and 0.66 g (4.8 mmol) potassium carbonate in 3.0 mL dimethylformamide, and stirred for 2 days at 25 °C, resulting in a pale yellow solution. Water is added and the precipitated materials are collected by filtration. The solid mixture obtained is fractionally crystallized from ethanol into which water is diffused producing very few colorless prisms of open oxime salt potassium 5,6-dimethoxy-2-(*N*-hydroxyimino) methanoylbenzoate (**8**). This is followed by the major product, long colorless needles, mp 95 °C of **10**. A very small amount of colorless prisms of 5,6-dimethoxyphthalimide (**9**) are also obtained. Each was characterized by X-ray crystallography (vide infra) though there was insufficient sample to obtain spectral data for **8** and **9**. Analysis for **10**: ^{1}H-nmr CD_3OD, 26 °C: δ7.78, d, 1H, aryl-H; δ 7.40, d, 1H, aryl-H; δ 4.8, s, 1H, OH; δ 3.97, s, 3H, OMe; δ 3.75, s, 3H, OMe; ^{13}C-nmr: CD_3OD, 26 °C: δ 169.7, C=O; δ 162.9, C=O; δ 156.3, 144.5, 132.8, 127.6, 120.9, 119.5, aryl C's; δ 60.3, 55.2, OMe's; IR (solid, cm^{-1}): 3224 broad, νOH; 2947, 2843, νCH; 1699 (s), νC=O; 1598, 1493 aryl νC=C; 1263 (s), νC–O.

3-Chloro-4,4-dimethylisobenzopyran-1-one (**11**)

To 1.00 g (4.8 mmol) 3-hydroxy-4,4-dimethylisobenzopyran-1-one (**3**) was added 1.5 mL (2.46 g, 20.7 mmol) thionyl chloride, and the mixture was stirred and heated to 45 °C for 2 days. Excess thionyl chloride was removed under reduced pressure, and the residue (1.01 g, 99 %) eventually crystallized as large colorless prisms, mp 82–85 °C. Analysis: ^{1}H-nmr (CD_3OD): δ 7.98, d, 1H; δ 7.51, t, 1H; δ 7.33, d, 1H; 7.26, t, 1H; δ .446, s, 1H, pseudoacyl-H; δ 1.32, s, 3H, methyl; 1.27, s, 3H, methyl; ^{13}C-nmr: δ 165.773, C=O; δ 146.783, 134.624, 130.017, 127.056, 124.786, 123.313, aryl-C's; δ 102.165, pseudoacyl C; δ 38.356, quaternary C; δ 26.465, 21.904, *gem*-dimethyl

Table 1 Relevant crystallographic information for **4**, **6**, **8**, **9**, **10** and **14** (esd's in parentheses)

	4	**6**	**8**
Formula	C_8 H_6 N_2 O_2	C_4 H_2 Cl_2 N_2 O_2	C_{10} H_{10} K N O_5
Formula weight	162.15	180.98	263.29
F(000)	336	360	544
Size (mm)	0.59 × 0.24 × 0.05	0.89 × 0.37 × 0.14	0.29 × 0.17 × 0.05
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	P 2_1 2_1 2_1	P −1	P $2_1/c$
Cell constants (temp., K)	101(2)	298(2)	298(2)
a (Å)	3.7784(6)	7.2634(7)	8.6002(5)
b (Å)	9.0723(15)	7.6485(11)	20.3845(14)
c (Å)	20.514(2)	12.2085(11)	6.5027(4)
α (°)	90.000	93.523(10))	90.000
β (°)	90.000	98.001(8)	92.933(6)
γ (°)	90.000	101.844(11)	90.000
Volume ($Å^3$)	703.21(18)	654.5(1)	1,138.50(12)
Z, density (Mg/m^3)	4, 1.532	4, 1.847	4, 1.536
μ (mm^{-1})	0.114	0.921	0.475
Data, R_{merge}	4128, 0.0282	6612, 0.0452	6815, 0.0499
Unique data, $I > 4\sigma_I$	2153, 1831	4011, 2455	3488, 1248
Completeness (%), max. θ	99.8, 30.57	99.8, 30.50	99.9, 30.50
R, wR (unique data)	0.051, 0.089	0.180, 0.390	0.174, 0.144
R ($I > 4\sigma_I$)	0.039	0.152	0.0619
Parameters, restraints	110, 0	183, 0	157, 1
Goodness-of-fit	1.002	1.026	1.009
Δρ(final) ($e/Å^3$)	0.37, −0.29	2.22, −1.05	0.30, −0.63
	9	**10**	**14**
Formula	C_{10} H_9 N O_5	C_{10} H_9 N O_4	C_{11} H_{14} N_2 O_3
Formula weight	223.18	207.19	222.24
F(000)	464	432	472
Size (mm)	0.40 × 0.04 × 0.02	0.40 0.35 0.10	0.35 × 0.26 × 0.08
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	P 2_1 2_1 2_1	P $2_1/c$	P $2_1/c$
Cell constants (temp., K)	298(2)	298(2)	101(2)
a (Å)	3.9579(3)	14.9948(11)	13.1638(3)
b (Å)	15.5058(11)	8.4383(4)	6.3069(2)
c (Å)	15.8646(14)	7.2942(5)	13.4581(3)
β (°)	90.000	95.638(6)	108.256(3)
Volume ($Å^3$)	973.6(1)	918.47(10)	1061.09(5)
Z, density (Mg/m^3)	4, 1.523	4, 1.498	4, 1.391
μ (mm^{-1})	0.124	0.118	0.102
Data, R_{merge}	3950, 0.0399	9324, 0.0191	9809, 0.0262
Unique data, $I > 4\sigma_I$	2155, 887	2819, 1877	3251, 2352
Completeness (%), max. θ	90.5, 28.55	99.9, 30.57	99.7, 30.61
R, wR (unique data)	0.1286, 0.0385	0.0647, 0.0991	0.0625, 0.0877
R ($I > 4\sigma_I$)	0.0375	0.0437	0.0396
Parameters, restraints	146, 0	136, 0	152, 0
Goodness-of-fit	0.837	1.004	1.005
Δρ(final) ($e/Å^3$)	0.15, −0.14	0.63, −0.16	0.34, −0.28

C's; IR: (solid, cm^{-1}): 3072 (w), aryl νCH; 2975 (w), νCH; 1722 (s), νC=O; 1604 (m) aryl νC=C; 1452 (m), 1373 (m), δ HCH; 1,265 (s), νC–O; 703 (s) νC–Cl.

2-Hydroxy-3-(hydroxyamino)-4,4-dimethyl-3H-isoquinolin-1-one (**14**)

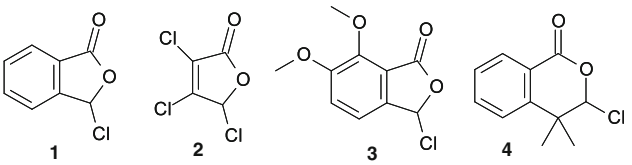
To 0.050 g **11** dissolved in 1.0 mL of 95 % ethanol was added 0.164 g (2.36 mmol) hydroxylamine hydrochloride and 0.489 g (3.54 mmol) potassium carbonate. The mixture was stirred for 3 days at 60 °C. Then 0.088 g (1.27 mmol) hydroxylamine was added, and the mixture stirred for another day, giving a colorless or very slightly yellow solution with some insoluble salts. The solvent was evaporated under an air stream, and the residue dissolved in ethanol and filtered from the salts. On slow evaporation, large colorless hexagonal crystals of **14** separate, mp about 160 °C with gas evolution and decomposition. Compound **14** is insoluble in water, acetone, acetonitrile or chloroform, but soluble in methanol. Analysis: ^{1}H-nmr (CD_3OD): δ 7.882, 7.863, d, 1H, aryl peri-H; δ 7.375, t, 1H; aryl-H; δ 7.29, m, 2H; aryl-Hs; δ 4.754, s, 2H, OHs; δ 4.206, s, 1H, pseudoacyl-H; δ 1.47, s, 3H, methyl; δ 1.28, s, 3H, methyl; ^{13}C-nmr: δ 163.3, C=O; δ 146.2, 132.0, 127.1, 126.5, 125.9, 123.4, aryl-C's; δ 85.9, pseudoacyl C; δ 38.4, quaternary C; δ 31.3, 21.8, *gem*-dimethyl C's. IR (solid, cm^{-1}): 3258 (m, broad), νNH; 3177 (m, broad), νOH; 3063 (w), aryl νCH; 2983 (m), νCH; 1698 (s); νC=O.

Crystallography

Single crystals of **4**, **6**, **8–10**, **14** were chosen for crystallographic study with Mo Kα radiation (λ = 0.71073 Å). Data were collected on an Oxford Gemini system. Relevant details of the crystallographic experiments are given in Table 1. The structures were solved with SHELXS-86 [13], and refined with SHELXL-97 [14]. All non-H atoms were found in initial E-maps, and were refined with attendant anisotropic librational parameters. H-atoms on carbons were assigned calculated locations; some H-atoms on nitrogens and oxygens were located in the different fourier maps, and their positions were refined with the usual foreshortened N–H and O–H lengths. Computed metrics involving Hs use uncorrected (foreshortened) N–H and O–H locations. All Hs were assigned isotropic librational parameters equal to 120 % of the U_{eq} of the attached atoms. No corrections for extinction were found to be necessary. For structure **6**, crystals are invariably multiple or twinned. After examination of a number of specimens, the best that could be found had a major domain with at least five other recognizable similar and disoriented components. The structure has been solved but the diffraction pattern was considerably affected by intensity from other domains; the results are poor, but included here for completeness.

Discussion

Pseudoacid systems chosen for study include three which favor the cyclic furanoid forms (*o*-formylbenzoic acid, mucochloric acid and opianic acid) and one dehydration resistant cyclic arylpyran (3-hydroxy-4,4-dimethylisobenzopyran-1-one). Since the pseudoacid forms are somewhat unreactive, we elected to employ their pseudoacyl chlorides instead so that less stringent reaction conditions could be pursued. An excess of hydroxyamine hydrochloride was reacted with 3-chloroisobenzofuran-1-one (**1**), mucochloryl chloride (**2**), opianyl chloride (**3**), and 3-chloro-4,4-dimethylisobenzopyran-1-one (**4**) and potassium carbonate.



The choice of base is important in these reactions, since use of pyridine or triethylamine usually leads to decomposition. Cleaner reactions have resulted from use of sodium carbonate or potassium carbonate. Compounds **1**, **2** and **4** are only slowly hydrolyzed in polar solvents with water present, so 95 % ethanol could be used in the reactions. Opianyl chloride is more rapidly hydrolyzed, so dimethylformamide was used as a replacement. Diffraction methods were used to complement other spectroscopic identifications, since oxime products were difficult to identify from spectroscopy alone.

Reaction of **1** produced the hydroxyimino/amide **4** (Fig. 1), formation of which involves oxidation of the pseudoacid and two equivalents of hydroxylamine. We

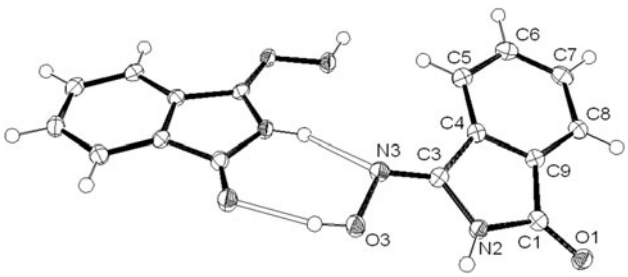
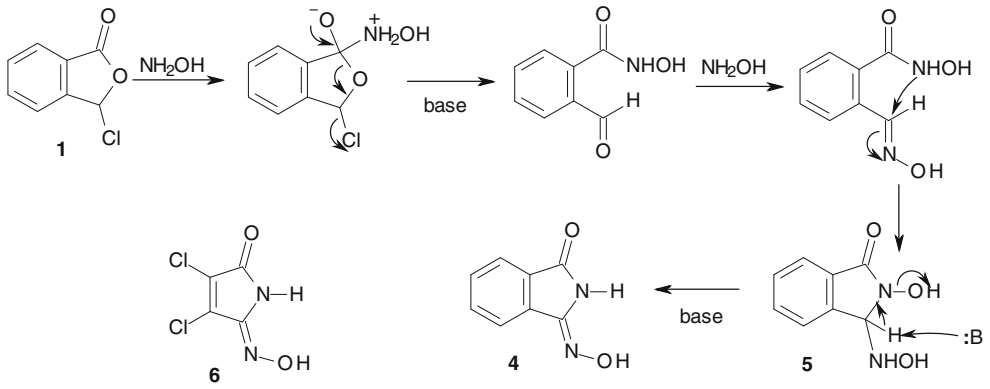


Fig. 1 Thermal ellipsoid plot (50 % enclosures) of **4** showing intermolecular H-bonds

speculate that the reaction proceeds through an intermediate hydroxyamino/hydroxyamide **5**, which then undergoes dehydration/oxidation.



Crystals of **4** are large well formed colorless prisms from ethanol, mp 255.9–257.3 °C. Molecules are nearly planar, with only the hydroxy group very slightly departing from the plane described by the remaining eleven non-H atoms of the molecule. In the crystal, molecules for intermolecular hydrogen-bonds with two neighbors using both the hydroxyimino and cyclic imide functions. The resulting $C_1^1(7)$ [15] chains link the planar molecules (using planes described by the ring and carbonyl oxygen atoms), forming pleats or corrugations with an interplanar angle of 21.7(1)° and every other molecule parallel with their mean planes displaced by 1.7 Å perpendicular to the planes. Between pairs of molecules, the three atom=N–O–H group donates and accepts hydrogen-bonds from the four atom *Z*-imide H–N–C=O group, forming a ring with $R_2^2(7)$ pattern. Hydroxyl donates to carbonyl with O···O distance 2.720(2) Å and angle at H 165°, and imide donates to imine with N···N distance 2.920(2) Å and angle at H 146°. The imine N is *syn* to the imide NH coplanar suggesting that an intramolecular N–H···O hydrogen-bond is present; for this N···O is 2.624(2) Å, and the angle at H is 93°. A weak intermolecular C–H···O(carbonyl) hydrogen bond may also be present with C···O 3.337(3) Å, angle at H 139.5(4)°. The hydroxyimino C=N is 1.278(2) Å, the amide C_{acyl}–N is 1.381(2) Å, the other C–N is 1.397(2) Å. The carbonyl C=O is 1.224(2) Å. These are generally in agreement with typical values for these bonds [16]. Aryl ring C–C bonds are similar with a mean distance 1.392 Å and a range of ±0.004 Å, with C4–C5 1.390(2) Å, C4–C9 1.395(2) Å, C5–C6 1.393(2) Å, C6–C7 1.396(2) Å, C7–C8 1.390(2) Å, C8–C9 1.388(2) Å.

A similar product is isolated from the reaction of mucochloryl chloride (**2**) and hydroxylamine. This hydroxyimino/amide (**6**, Fig. 2), also involves oxidation of the pseudoacid and two equivalents of hydroxylamine. Two molecules comprise the asymmetric unit of the triclinic structure (P-1), a molecules are essentially planar and arranged in sheets in which weak intermolecular Cl···Cl interactions (at 3.44(2) and 3.46(2) Å) alternate with intermolecular hydrogen-bonding within the sheets. These sheets closely match the [201] crystal planes (d_{201} = 3.24 Å), and F_{201} = 238, 66 % of the F_{000} = 359. This feature provides an explanation for the multiple or twinned occurrence of the crystals, with crystal domains parallel to and disoriented relative to these dominant packing planes. hydrogen-bonding links molecules within the sheets and in chains. The hydroxyimine is linked in chains to the carbonyl O with O···O distances 2.78(2) and 2.79(2) Å, and angle at H 158° and 144°. The imine N is *syn* to the imide NH coplanar suggesting that an intramolecular N–H···O hydrogen-bond is present; for this N···O is 2.60(2) and 2.61(2) Å, and the angle at H is 93° and 92°. Within sheets, imides form complementary hydrogen-bonds around inversion centers, with N···O distances of 2.88(1) and 2.87(1) Å, and angles at H 167° and 169°.

In contrast to the two systems just described, opianyl chloride **7** forms several products on reaction with hydroxylamine and a carbonate base in DMF. All of these

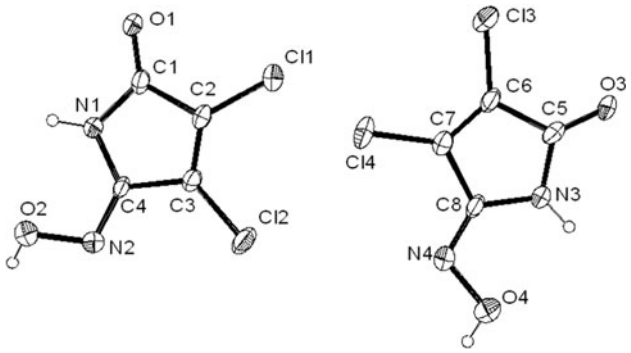
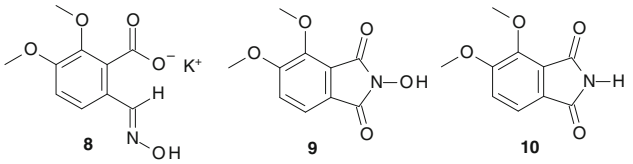


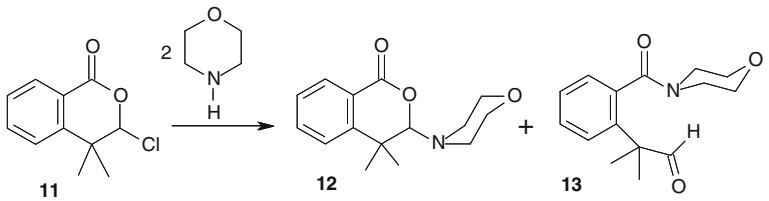
Fig. 2 Thermal ellipsoid plot (30 % enclosures) of **6**

products are polar and quite soluble in ethanol though less soluble in water. Careful fractional crystallization has permitted separation, and solubility and crystal morphology allow the phases to be distinguished. First, a minor component which is least soluble in ethanol separates; it is the potassium salt of the open oxime, or potassium 5,6-dimethoxy-2-(*N*-hydroxyimino)methanoylbenzoate (**8**, Fig. 3). It is followed by the major product *N*-hydroxyimide (**9**, Fig. 4), and then another minor component, the imide of hemipinic acid (**10**, Fig. 5). An hydroxyimino/amide product related to **4** or **6** was not found.



Bond lengths and angles for **8–10** are in normal ranges [16].

In the three furanoic pseudoacyl systems just described, all three show products with hydroxylamine and a carbonate base which have undergone oxidation. To examine the results in an arylpyran system, we employed the dehydration resistant system 3-hydroxy-4,4-dimethylisobenzopyran-1-one (**3**), beginning with its pseudoacyl chloride (**11**). Arylfuran pseudoacyl halides react with secondary amides to form tertiary pseudoamides [4]. Similarly, following the usual procedure with exactly two equivalents of morpholine, **11** reacts to form a pseudomorpholinamide (**12**), an equal amount of an unexpected open aldehyde/secondary morpholinamide (**13**) and an equivalent of morpholinium chloride. The oily aldehyde/amide **13**, after chromatographic separation, was reacted with excess hydroxylamine in an attempt to form a solid derivative oxime.



Salt **8** is centrosymmetric and monoclinic. Potassium ions coordinate to six Os (at 2.73, 2.74, 2.84, 2.89, 2.94, 3.36 Å), and one N atom (3.11 Å). Each O, including the methoxy Os coordinate K^+. Hydroxyimino Os donate a hydrogen-bond to carboxylate O, with O···O 2.63(1) Å, and angle at H 178°. *N*-Hydroxyimide **9** forms slender orthorhombic needles from ethanol/water. Molecules are hydrogen-bonded in $C_1^1(5)$ chains with hydroxyl donors and carbonyl acceptors, O···O 2.66(1) Å, angle at H 156°. This carbonyl also has a close contact with a methoxy carbon, C···O 3.08(1) Å. The second carbonyl has an intermolecular close contact with a aryl carbon, C···O 3.29(1) Å.

The imide of hemipinic acid **10** is centrosymmetric and monoclinic, and molecules form sheets through hydrogen-bonding interactions, with the sheets parallel to and approximately between the crystal [10−1] planes. In the sheets, molecules form hydrogen-bonds in $C_1^1(4)$ chains with imide N–H donors and one of the two carbonyl Os, with N···O 3.03 Å, angle at H 162°. This carbonyl O also accepts a weak (aryl)C–H···O contact, with C···O 3.39 Å, angle at H 168°. The other carbonyl O also accepts a weak (aryl)C–H···O contact, with C···O 3.32 Å, angle at H 158°.

The product in this reaction was a colorless solid which instead no longer retained the morpholine group. Single-crystal X-ray diffraction revealed a centrosymmetric monoclinic structure for **14** as a *N*-hydroxyamide/hydroxylamine in which clearly two equivalents of hydroxylamine have reacted with the pseudoacyl system (Fig. 6). This material is analogous to the putative intermediate **5** in the *o*-formylbenzoic acid scheme. Compared to the

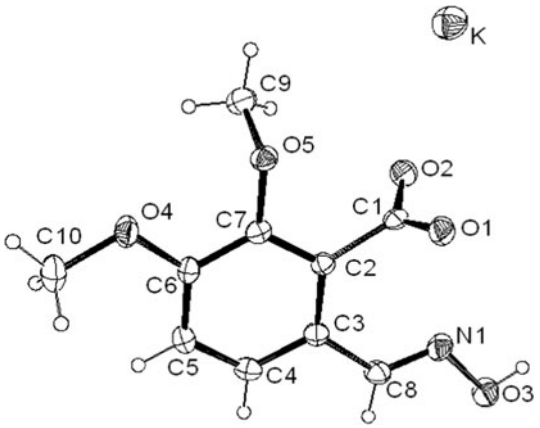


Fig. 3 Thermal ellipsoid plot of potassium salt **8** (30 % enclosures)

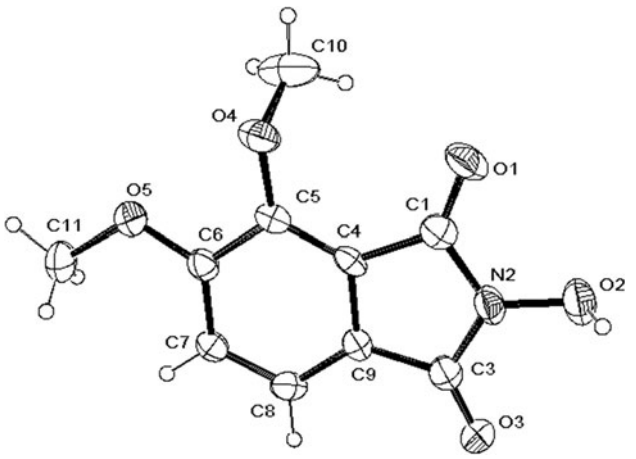


Fig. 4 Thermal ellipsoid plot (30 % enclosures) of *N*-hydroxyimide of opianic acid, **9**

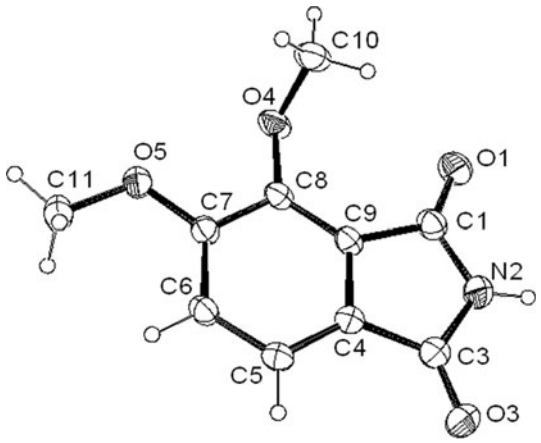


Fig. 5 Thermal ellipsoid plot (30 % enclosures) of **10**

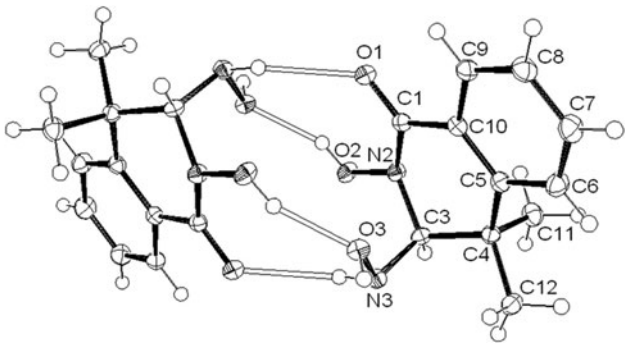
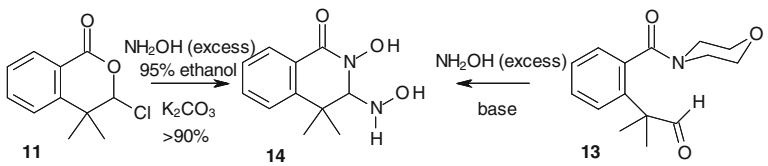


Fig. 6 Thermal ellipsoid plot (50 % enclosures) of **14** showing complementary intermolecular H-bonds

pseudoacid ($C_{11}H_{12}O_3$) from which **14** is derived, its formula $C_{11}H_{14}N_2O_3$ represents a gain of N_2H_2. Since typical aldehydes/ketones gain NH on forming their oximes, we describe **14** and putative intermediate **5** as pseudo-oximes. The pseudoacyl carbon is not oxidized in these transformations, and it retains two bonds to N(OH) groups, in an analogy to normal *N*-hydroxyimines (oximes). It proved difficult to reproduce the yields of **14** by this synthetic method, and use of tertiary amines gave very dark reaction products from which **14** could not be retrieved. Since **11** is soluble but does not react with aqueous ethanol, we reacted **11** with excess hydroxylamine hydrochloride in 95 % ethanol and potassium carbonate or sodium carbonate at 60 °C. This produced pseudo-oxime **14** cleanly and quantitatively.



Crystals of **14** are well-formed hexagonal tablets which grow large [001] and [00−1] faces, bounded by [100], [−100] and [010], [0−10]. The dehydration that apparently occurs readily in the (aryl)furan systems requires heating to above 160 °C for **14**. Both *N*-hydroxyamide and hydroxyamino groups engage in pairwise complementary intermolecular hydrogen-bonding. The five-atom hydroxyamide O=C–N–O–H donates and accepts hydrogen-bonds from the three atom hydroxyamino H–N–O group (Fig. 6), forming rings with pattern $R_2^2(8)$. A longer path, $R_2^2(12)$, can also be described between these groups. Thus, there are four intermolecular hydrogen-bonds, two complementary N···O [3.008(1) Å; angle at H 144°] and two complementary O···O [2.685(1) Å; angle at H 153°]. Additionally, molecules form infinite chains along *b* by intermolecular O–H···O hydrogen-bonds between hydroxyamino O donors and carbonyl O acceptors, with O···O 2.696(1) Å and with angle at H 175°.

The molecular structure shows the pseudoacyl hydroxyamino group disposed axially. The endocyclic C–N(OH) distance is 1.462(2) Å, and the exocyclic C–N(OH) distance is 1.448(2) Å. The exocyclic C–N is shorter by 0.014 Å, suggestive of the usual bond disparities found in α-anomeric systems. The magnitude of the difference is much smaller than that observed in pseudoacids, which

have the O–C–O anomeric sequence and a C–O bond length disparity of about 0.08 Å. The orientation of the hydroxyamino group places the non-bonding electron pair on N synclinal with the adjacent endocyclic C–N bond, a conformation consistent with $n_N \rightarrow \sigma^*_{C-N}$ donation, and associated with an operative exo-anomeric effect. A recent review of oximes and hydroxylamines shows no references to a similar pair of adjacent functions [17].

Conclusions

Furanoid pseudoacyl chlorides react with hydroxylamine to form oxidized imide products which may form through dehydration of an intermediate pseudo-oxime. A dehydration resistant arylpyran pseudoacyl chloride forms a stable pseudo-oxime (*N*-hydroxyamido/hydroxylamine) with hydroxylamine and a carbonate base.

Supplementary Materials

Crystallographic information files have been deposited with the Cambridge Crystallographic Data Centre for crystal structures **4** (860347), **6** (860348), **8** (860349), **9** (860350), **10** (860351), **14** (860352). CCDC data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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Conflict of interest The authors declare that they have no commercial conflicts of interest.

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