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ORIGINAL PAPER

Anhydrides of Arylfuran and Arylpyran Pseudoacids: Formation and Structures; C–O Bond Lengths Trends in Pseudo *o*-Formylbenzoic Acid Derivatives

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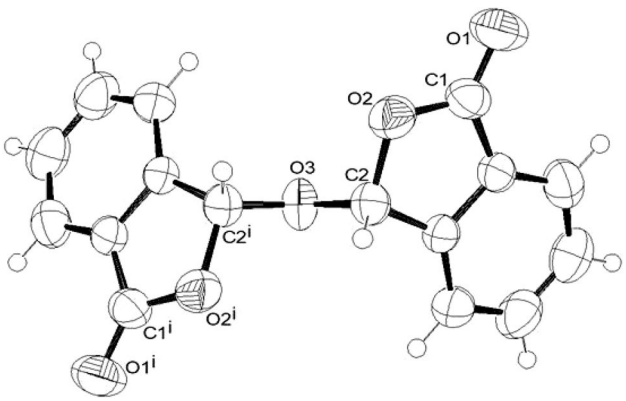
Abstract
Three methods for producing anhydrides of arylfuran and arylpyran pseudoacids were explored. These included thermal dehydration, phosgene or thionly chloride activation and decomposition, and dicyclohexylcarbodiimide activation and coupling. Derivatives of the cyclic forms of *o*-formylbenzoic acid, *o*-acetylbenzoic acid, 2-carboxyphenylacetaldehyde and of 4,4-dimethyl-3,4-dihydro-3-hydroxy-[1H]-isobenzopyran-1-one were formed including dipseudoanhydides and normal-pseudo anhydrides. Crystal and molecular structures for *meso* and (*R,R/S,S*)-bis(1[3H]-isobenzofuranone-3-yl) ether, (*R,R/S,S*)-bis(3-methyl-1[3H]-isobenzofuranone-3yl)ether, *meso* (3,4-dihydro-[1H]-isobenzopyran-1-one-3-yl)ether, 3-benzoyloxy-1[3H]-isobenzofuranone, 3-benzoyloxy-3-methyl-1[3H]isobenzofuranone, 3-(4′-nitrobenzoyloxy)-4,4-dimethyl-3,4-dihydro-[1H]-isobenzopyran-1-one, and (1[3H]-isobenzofuranone-3-yl)(4,4,dimethyl-3,4-dihydro-[1H]-isobenzopyran-1-one-3-yl)ether are reported. Endocyclic pseudoacyl C–O bonds are always longer than the exocyclic pseudoacyl C–O bonds. It is possible to refine the previously established C–O bond length dependencies on the pK_a (of the conjugate acids) of the leaving groups for 3-substituted 1-[3H]-isobenzofuranones. Of six dipseudoanhydrides studied, conformations are found with exocyclic C–O(ether) linkages synclinal to the endocyclic C–O and away from the ring (*exo* conformation) in two *meso* structures, two of three RR/SS forms and in a chiral unsymmetrical form. An *endo* conformation is observed in one of the RR/SS forms. In three normal-pseudo anhydrides, both *endo* and *exo* conformations are observed.

Graphic Abstract
Synthetic methods for formation of anhydrides of several arylfuran and arylpyran pseudoacids are described, and the pseudoacyl C–O bond length trends are determined for leaving groups spanning over 30 pK_a units.



Keywords Pseudoacids · Anhydrides · Coupling reactions · C–O bonds · Bürgi-Dunitz angle

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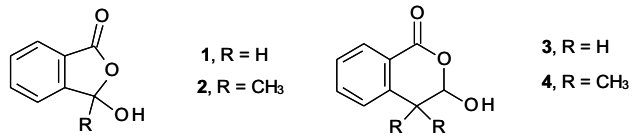
Introduction

The derivative chemistry of cyclic oxocarboxylic acids (pseudoacids) is regiochemically and stereochemically more varied than that of (normal) carboxylic acids. Functions corresponding to carboxylic acid derivatives are possible for the pseudoacyl group and include anhydrides which can be symmetric or unsymmetric, and dipseudo or normal-pseudo [1, 2]. This paper describes anhydrides formed by pseudoacids in many of these variants. Cyclization of oxocarboxylic acids introduces the lactol chiral center, so derivative pseudoacid anhydrides are necessarily composed of enantiomers or diastereomers [3, 4]. Methods for the formation of pseudoacyl anhydrides have received relatively little attention. In some systems, intramolecular dehydration may be favored, as in possibly the first and well known example of levulinic acid and its dehydration to α-angelicalactone [5, 6]. For oxocarboxylic acids with relative thermal stability, as in *o*-formylbenzoic acid (3-hydroxy-1(3H)-isobenzofuranone), intermolecular dehydration to a mixture of symmetric dipseudoanhydrides has been accomplished thermally [2, 7]. A symmetric normal-pseudo anhydride was produced from open *o*-benzoylbenzoic acid and cyclic *o*-benzoylbenzoyl chloride promoted with a base [2, 8, 9]. This oxocarboxylic acid system does not favor cyclic forms probably limiting general application of this method [10]. In the present study, several coupling methods are explored using simple benzofuran and benzopyran pseudoacids and benzoic acids. The structures have been determined to examine the O–C_{sp3}–O–C_{sp3}–O sequences at the centers of dipseudoanhydrides, and the O–C_{sp3}–O sequences of normal-pseudo anhydrides. Systematic studies of C_{sp3}–O bond-containing species are useful in light of the inherent variability in its bond metrics which in a recent extensive theoretical study of C–O bond lengths concluded that the large range of C–O lengths is explained by an approximately linear dependency with its bond critical point density. It is often easier to explain variations than predict them, with comparisons among similar compounds being most useful [11]. For selected pyranoid and furanoid systems, there have been several studies of C–O bond length trends [2, 12–14].

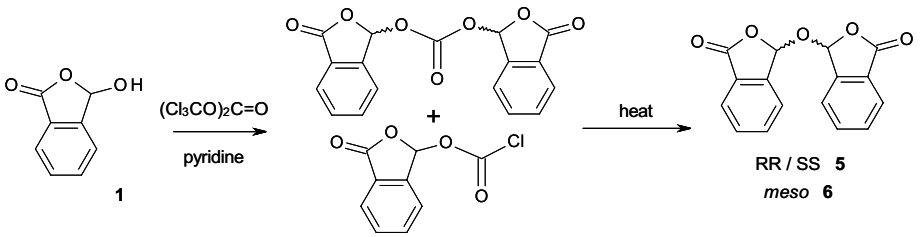


Scheme 1 Structures of 3-hydroxy-1(3H)isobenzfuranone (**1**), 3-hydroxy-3-methyl-1(3H)-iso benzofuranone (**2**), 3-hydroxy-3,4-dihydro-[1H]-isobenzopyran-1-one (**3**), and 3-hydroxy-3,4-dihydro-4,4-dimethy-[1H]-isobenzopyran-1-one (**4**), Cooper's pseudoacid [15]

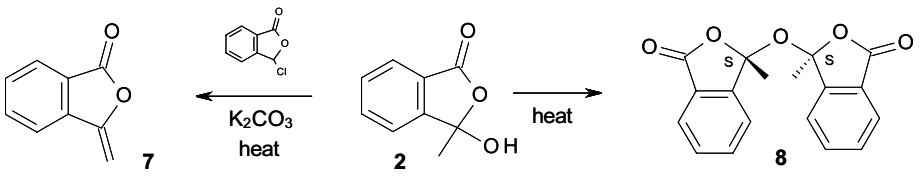
In Scheme 1, the structures are given for the four pseudoacids for which pseudoanhydride chemistry is explored. Compounds **1** and **4** are relatively resistant to elimination reactions, while **2** and **3** are susceptible to intramolecular dehydration to form unsaturated lactones or cyclic anhydrides.

Method A

Thermal dehydration. Pseudoacid **1** can be dehydrated directly by heating to 257 °C to the racemic (*R,R/S,S*) dipseudoanhydride, **5** and the *meso* (*R,S/S,R*) dipseuodanhydride, **6** [2]. Phase **5** forms colorless needles, mp 216 °C, which occur in the monoclinic system, space group I 2/*a*. Phase **6** forms colorless plates, mp 234 °C, also in the monoclinic system, space group P *n*. Phase **6** has also been obtained by thermal decomposition of the chloroformate of 3-hydroxy-1(3H)isobenzofuranone, which was formed from the pseudoacid (**1**), triphosgene and pyridine [16]. On heating above 90 °C, the chloroformate undergoes an exothermic reaction, as monitored by differential scanning calorimetry.

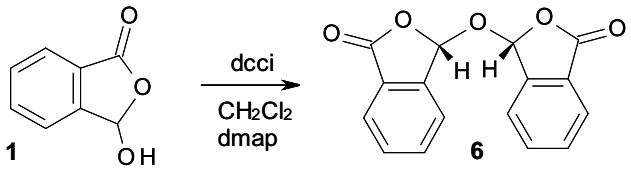


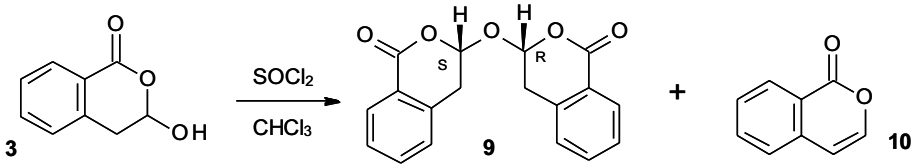
Pseudoacid **2** is somewhat susceptible to intramolecular dehydration. Where **2** is heated with a pseudoacyl halide and a base, the unsaturated lactone **7** is recovered [16]. Pseudoacid **2** can be dehydrated thermally to form the diastereomeric dipseudoanhydrides, from which the (*R,R/S,S*) isomer (**8**) was isolated in low yield.



Method B

Through the pseudoacyl halide. Pseudoacid **3** is sensitive to intramolecular thermal dehydration, and it reacts with thionyl chloride in chloroform solvent to form chiefly the *meso*-dipseudoanhydride (**9**) and isochromenone (**10**).

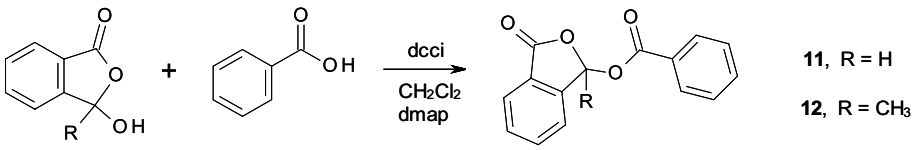




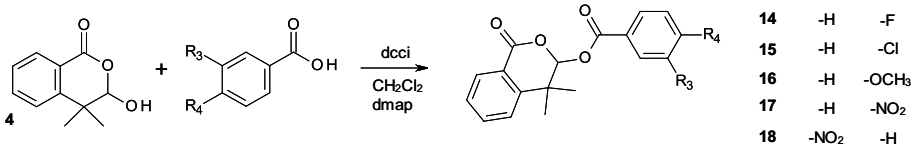
Method C

Using dicyclohexylcarbodiimide (DCCI). Compound **1** is a relatively unhindered pseudoacid, and it forms an "active ester" with DCCI which can be displaced by a second pseudoacid. The *meso*-dipseudoanhydride (**6**) was isolated from the reaction.

To form unsymmetric normal-pseudo anhydrides, DCCI coupling was generally effective. Pseudoacids **1** and **2** react with the active ester formed from benzoic acid to form the corresponding enantiomeric anhydrides.

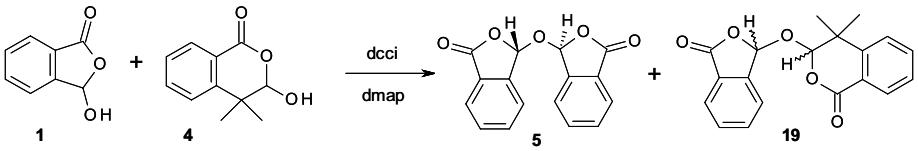


In a third example pseudoacid **4** reacts with the active esters of (substituted) benzoic acids forming the normal-pseudo anhydrides **13**–**18**. These are mostly oils, but compounds **15** and **17** crystallize.



	R_3	R_4
13	-H	-H
14	-H	-F
15	-H	-Cl
16	-H	$-OCH_3$
17	-H	$-NO_2$
18	$-NO_2$	-H

Lastly, an attempt to produce an unsymmetric dipseudoanhydride was pursued with the pseudoacids least likely to undergo dehydration (**1**, **4**). In this fourth example using the coupling method, a mixture of non-polar products were isolated from which (*R,R/S,S*)-**5** crystallized first, followed by the mixed anhydride **19**.



The crystal and molecular structures of the anhydrides **5**–**11**, **12**, **17** and **19** have been determined, and the metrics of the pseudoacyl linking groups have been examined. These are compared with the limited literature available.

Experimental

NMR on a Bruker 400 MHz instrument using tetramethylsilane as standard. DSC on a Shimadzu DSC-5. IR on a Perkin-Elmer FTIR. Most reagents were purchased from TCI America or Sigma Aldrich, and used as received. Pseudoacids **1** and **2** were commercially available. Compounds **3** and **4** were prepared by literature methods [15, 16].

Bis(1[3H]-isobenzofuranone-3-yl)ethers, (*R,R/S,S*)-5 and *meso*-6

A solution of 255 mg (1.70 mmol) of **1** in 8 mL dichloromethane was combined under N_2(g) with 250 mg (0.085 mmol) triphosgene. Then, 69 µL (0.085 mmol) pyridine was added slowly over 30 min. The reaction mixture warmed. After 1.5 h, water was added, and the organic layer was removed and evaporated *in vacuo*. The semi-solid material obtained was recrystallized from benzene. A colorless solid was obtained, mp 78.5 °C (DSC peak), having IR (cm^{-1}): 1786, 1763, 1741 (ν C=Os). On heating the solid to 155 °C (sand bath), gases were evolved and the orange solid obtained was recrystallized from ethyl acetate producing two distinct phases: colorless needles, *meso* form **6**, IR (cm^{-1}): 1771, (ν C=O), mp 218 °C (DSC peak), and colorless plates, (*R,R/S,S*) form **5**, IR (cm^{-1}) 1778, (ν C=O); mp 234 °C (DSC peak). Both phases were also obtained by thermal dehydration of **1** by heating to 250 °C, cooling and recrystallizing the solid residue from ethyl acetate [18]. Additionally, an anhydride was obtained from reaction of **1** with an equivalent of dicyclohexylcarbodiimide (DCCI) in CH_2Cl_2 at 0 °C to which was added a small amount of 4-dimethyl aminopyridine (DMAP, see preparation of **11**–**17**). Anhydride has R_f about 0.75 (TLC: silica, $CHCl_3$:EtOAc 10:1) and after isolation by chromatography, the major product proves to be polymorphs of the (*R,R/S,S*) form **5** (**5a**, prisms; **5b** rod-like needles). ^{1}H-NMR ($CDCl_3$, 25 °C), δ_H: 7.85, d, 2H, aryl–H; 7.65, t, 2H, aryl–H; 7.60, d, 2H, aryl–H; 7.45, d, 2H, aryl–H; 6.90, s, 2H, Ps–H; ^{13}C-NMR ($CDCl_3$, 25 °C), δ_C: 168.14, C=O; 144.10, 137.87, 131.09, 126.65, 124.69, 123.92, Ar–C's; 99.05, Ps-C. For **5a** and **5b,** IR: (cm^{-1}): 1769 cm^{-1}, (ν C=O).

3-Methano-1[3H]-isobenzofuranone, 7

This material was produced as one of the products of the reaction of 113 mg (0.689 mmol) 3-methyl-3-hydroxy-1[3H]-isobenzofuranone (**2**) with 116 mg (0.690 mmol) 3-chloro-3-hydroxy-1[3H]-isobenzofuranone and 200 mg (1.4 mmol) potassium carbonate in 8 mL dimethylformamide at 120 °C for 5 h. On cooling and removal of the insoluble materials and the solvent, a somewhat volatile colorless solid was isolated, IR: 1780 cm^{-1} (ν C=O), 1662 cm^{-1} (ν C=C). ^{1}H-NMR ($CDCl_3$, 25 °C) δ_H: 7.4–7.8, m, 4H, aryl–H; 4.50, s, 2H, $=CH_2$.

Bis(1[3H]-isobenzopyranone-3-yl)ether, *meso*, 9

To a solution of 3-hydroxy-[3H]-isobenzopyran-1-one [2-(2′oxoethyl)benzoic acid] in chloroform, one equivalent of thionyl chloride was added at room temperature. After standing 3 h, the solvent was slowly evaporated precipitating a colorless solid. On recrystallization from ethyl acetate, the anhydride forms colorless crystals (yield undetermined). IR: 1765 cm-1 (ν C=O); ^{1}H-NMR ($CDCl_3$, 25 °C) δ_H: 7.4–7.8, m, 8H, aryl–H; 4.50, d, 4H, CH_2; 5.55, t, 2H, Ps–H. From the residue of the recrystalization, the [1H]-isochromen-1-one (**10**) was also recovered; IR: 1730 cm^{-1}, (ν C=O); mp 47 °C.

3-Benzoyloxy-1[3H]-isobenzofuranone, 11

Benzoic acid (50 mg, 0.43 mmol) was dissolved in 8 mL CH_2Cl_2, and one equivalent of DCCI (87 mg, 0.43 mmol) was added at 0 °C, and stirred for an hour. Then, *o*-formylbenzoic acid (**1**) (65 mg, 0.43 mmol) was added and a catalytic amount of DMAP, and the mixture was allowed to stand overnight at 4 °C. TLC (silica, $CHCl_3$:EtOAc 10:1) showed five components. The fastest running component (R_f 0.92) was the anhydride **11**. After filtering the dicyclohexylurea from the reaction mixture, and evaporating the solvent, a thick layer chromatogram was run on the chloroform soluble residue of the reaction, and the band at highest R_f was removed and extracted, producing a colorless solid from ethyl acetate. ^{1}H-NMR ($CDCl_3$, 26 °C), δ_H: 8.09, Ar–H_5, d, 1H; 7.78, Ar–H_6, t, 1H; 7.61, Ar–H_7, t, 1H; 7.99, Ar–H_8, d, 1H; 6.897, Ps–H, s, 1H; 7.695, Ph-*ortho*, d, 2H; 7.46, Ph-*meta*, t, 2H; 7.27, Ph-*para*, d, 1H. IR: 1777 cm^{-1}, ν(C=O) furanone; 1740 cm^{-1}, ν (C=O) acyl.

3-Benzoyloxy-3-methyl-1[3H]-isobenzofuranone, 12

Benzoic acid (50 mg, 0.41 mmol) was dissolved in 8 mL CH_2Cl_2, and one equivalent of DCCI (87 mg, 0.41 mmol) was added at 0 °C, and stirred for an hour. Then, *o*-acetylbenzoic acid (**2**) (68 mg, 0.41 mmol) was added along with a catalytic amount of DMAP, and the mixture allowed to stand overnight at 4 °C. TLC (silica, $CHCl_3$:ethyl acetate 10:1) showed five components. The fastest running component (R_f 0.9) was benzoic anhydride. Compound **12** had R_f 0.8. After filtering the dicyclohexylurea from the reaction mixture, and evaporating the solvent, a thick layer chromatogram was run on the chloroform soluble residue of the reaction, and the band at R_f 0.8 was removed and extracted, producing a colorless crystalline solid from ethyl acetate. ^{1}H-NMR ($CDCl_3$, 26 °C), δ_H: 8.147, Ar–H_5, d, 1H; 7.624, Ar–H_6, t, 1H; 7.482, Ar–H_7, t, 1H; 7.950, Ar–H_8, d, 1H; 2.121, Me, s, 3H; 8.118, Ph-ortho, d, 2H; 7.415, Ph-meta, t, 2H; 7.624, Ph-para, d, 1H. ^{13}C-NMR ($CDCl_3$, 26 °C), δ_C: 170.36, 163.81, C(=O)'s; 147.90, 134.58,130.66, 128.86, 125.58, 122.02, aryl-C's; 105.66, pseudoacyl-C; 25.25, methyl-C. IR: 1770 cm^{-1}, ν(C=O) furanone; 1730 cm^{-1}, ν (C=O) acyl.

3-Benzoyloxy-4,4-dimethyl-3,4-dihydro-[1H]-isobenzopyran-1-one, 13

The general method was as follows: In a 50 mL round bottom flask 50 mg (0.409 mmol) of benzoic acid was combined with 1 equivalent (84 mg, 0.409 mmol) of DCCI and enough dichloromethane at 0 °C (ice-bath) to dissolve the substances. The mixture was stirred for 1 h, then 1 equivalent of Cooper's pseudoacid (**4**, 79 mg, 0.409 mmol) was added all at once followed by a catalytic amount of DMAP. The mixture was stirred for 6 h at 0 °C. Dicyclohexylurea began to precipitate, and TLC (SiO_2, $CHCl_3$:EtOAc 10:1) showed two materials with R_fs > 0.7. After warming to room temperature, the DCU was removed by filtration, and the solvent volume reduced in an air stream. The product mixture was applied to a thick-layer chromatography plate (SiO_2), and eluted with $CHCl_3$:EtOAc 10:1. The R_f 0.88 material (fastest running) was compound **13**; R_f 0.77 was benzoic active ester. Compound **13** was a colorless oil. ^{1}H-NMR: ($CDCl_3$, 26 °C), δ_H: 8.149, Ar–H_8, d, 1H; 7.697, Ar–H_7, t, 1H; 7.555, t, Ar–H_6, t, 1H; 7.456, Ar–H_5, d, 1H; 1.492, methyls, s, 6H; 6.666, Ps–H, s, 1H; 7.839, Ph2′–H, d, 2H; 7.381, Ph3′–H, t, 2H; 7.445, Ph4′–H, t, 1H. ^{13}C-NMR ($CDCl_3$, 26 °C), δ_C: 123.096, C–(C=O); 145.564, C–(CMe_2); 124.336, C5; 134.745, C6; 127.526, C7; 130.4, C8; 164.385, C(=O); 97.894, Ps-C; 37.546, quat-C; 27.353, Me; 21.995, Me; 162.65, C(=O, phenyl); 130.4, C*ipso*; 129.865, C2′; 128.502, C3′; 133.777, C4′.

3-(*p*-Fluorobenzoyloxy)-4,4-dimethyl-3,4-dihydro-[1H]-isobenzopyran-1-one, 14

The method used to make compound **13** was followed here. The product with R_f 0.89 (SiO_2, $CHCl_3$:EtOAc; 10:1) was compound **14**, an oil. ^{1}H-NMR ($CDCl_3$, 26 °C), δ_H: 7.049, Ar–H_8, d, 1H; 7.049, Ar–H_7, t, 1H; 7.696, t, Ar–H_6, t, 1H; 8.141, Ar–H_5, d, 1H; 1.482, methyls, singlets, 6H; 6.642, Ps–H, s, 1H; 7.860, Ph2′–H, dd, 2H; 7.443, Ph3′–H, dd, 2H. ^{13}C-NMR ($CDCl_3$, 26 °C), δ_C: 123.019, C–(C=O); 145.479, C–(CMe_2); 124.909, C5; 134.791, C6; 128.131, C7; 130.415, C8; 163.417, C(=O); 97.972, Ps-C; 37.515, quat-C; 27.361, Me; 21.932, Me; 162.549, C(=O, phenyl); 132.460, C*ipso*; 127.565, C2′; 115.654, C3′; 167.436, C4′.

3-(*p*-Chlorobenzoyloxy)-4,4-dimethyl-3,4-dihydro-[1H]-isobenzopyran-1-one, 15

The product with R_f 0.94 (SiO_2, $CHCl_3$:EtOAc; 10:1) was compound **15**, a solid. ^{1}H-NMR ($CDCl_3$, 26 °C), δ_H: 7.463, Ar–H_8, d, 1H; 7.455, Ar–H_7, t, 1H; 7.690, t, Ar–H_6, t, 1H; 8.159, Ar–H_5, d, 1H; 1.483, methyl, s, 3H; 1.476, methyl, s, 3H; 6.639, Ps–H, s, 1H; 7.357, Ph-*ortho*, dd, 2H; 7.776, Ph-*meta*, dd, 2H. ^{13}C-NMR ($CDCl_3$, 26 °C), δ_C: 122.996, C–(C=O); 145.433, C–(CMe_2); 124.320, C5; 134.807, C6; 127.116, C7; 130.439, C8; 163.587, C(=O); 105.400, Ps-C; 37.515, quat-C; 27.369, Me; 21.940, Me; 162.495, C(=O, phenyl); 127.588, C*ipso*; 131.205, C2′; 128.913, C3′; 140.36, C4′.

Table 1 Crystallographic information on dipseudoanhydride structures **5**, **6, 8**, **9**, **19**

Compound	**5a**	**5b**	**6**	**8**	**9**	**19**
Formula	$C_{16}H_{10}O_5$	$C_{16}H_{10}O_5$	$C_{16}H_{10}O_5$	$C_{18}H_{14}O_5$	$C_{18}H_{14}O_5$	$C_{19}H_{16}O_5$
FW	282.25	282.25	282.25	310.30	310.30	324.33
Temp. (K)	297	297	296	296	295	110
Crystal system	Mono clinic	Ortho rhombic	Mono clinic	Mono clinic	Mono clinic	Tetragonal
Space group	C 2/*c*	P *bca*	P *n*	C 2/*c*	P $2_1/n$	I −4
a (Å)	13.8519(8)	6.0908(3)	4.448(2)	23.500(10)	14.125(22)	19.7930(3)
b (Å)	8.1410(4)	15.4037(8)	6.496(3)	8.393(3)	7.300(10)	19,7930(3)
c (Å)	11.7772(6)	27.6505(17)	22.227(9)	15.869(7)	15.148(32)	8.07666(16)
α (°)	90	90	90	90	90	90
β (°)	103.628(5)	90	91.32(5)	103.05(3)	97.24(15)	90
γ (°)	90	90	90	90	90	90
Volume (Å^3)	1298.70(12)	2494.2(2)	641.9(5)	3049(2)	1549(5)	3164.05(10)
Z	4	8	2	8	4	4
F_{000}	1168	584	292	1296	648	1360
d_{calc} (Mg/m^3)	1.445	1.453	1.460	1.352	1.330	1.362
Unique refl., $I>4\sigma_I$	1892, 1427	1980, 1529	1287, 914	3520, 2057	3572, 846	2781, 2742
Parameters, restraints	98, 0	191, 0	191, 2	209, 0	209, 1	335, 39
R_1 ($I>4\sigma_I$)	0.0305	0.0439	0.0479	0.0540	0.0671	0.0317
wR_2(all)	0.0681	0.1208	0.1088	01256	0.1214	0.0829
GooF	1.089	1.062	1.050	1.053	0.978	1.074
$\Delta\rho_{max,\ min}$ (e$^-$/Å^3)	+0.14, −0.11	+0.25, −0.16	+0.19, −0.23	+0.18, −0.17	+0.21, −0.21	+0.14, −0.19

Estimated standard deviations in parentheses

3-(*p*-Methoxybenzoyloxy)-4,4-dimethyl-3,4-dihydro-[1H]-isobenzopyran-1-one, 16

The product at R_f 0.84 (SiO_2, $CHCl_3$:EtOAc; 10:1) was compound **16**, an oil. ^{1}H-NMR ($CDCl_3$, 26 °C), δ_H: 7.486, Ar–H_8, d, 1H; 7.454, Ar–H_7, t, 1H; 7.689, t, Ar–H_6, t, 1H; 8.158, Ar–H_5, d, 1H; 1.483, methyl, s, 3H; 1.481, methyl, s, 3H; 6.644, Ps–H, s, 1H; 7.804, Ph2′–H, d, 2H; 6.860, Ph3′–H, d, 2H; 3.834, OCH_3, s. ^{13}C-NMR ($CDCl_3$, 26 °C), δ_C: 123.189, C–(C=O); 145.681, C–(CMe_2); 124.305, C5; 134.652, C6; 127.457, C7; 130.369, C8; 164.005, C(=O); 97.678, Ps-C; 37.569, quat-C; 27.299, Me; 21.963, Me; 162.781, C(=O, phenyl); 120.936, C*ipso*; 132.026, C2′; 113.795, C3′; 164.044, C4′; 55.437, OCH_3.

3-(*p*-Nitrobenzoyloxy)-4,4-dimethyl-3,4-dihydro-[1H]-isobenzopyran-1-one, 17

The product with R_f 0.83 (SiO_2, $CHCl_3$:EtOAc; 10:1) was compound **17**, a solid, recrystallized from ethyl acetate. ^{1}H-NMR ($CDCl_3$, 26 °C), δ_H: 7.718, Ar–H_8, d, 1H; 7.473, Ar–H_7, t, 1H; 7.488, t, Ar–H_6, t, 1H; 8.173, Ar–H_5, d, 1H; 1.508, methyls, s, 6H; 6.670, Ps–H, s, 1H; 8.222, Ph-2′–H, d, 2H; 8.015, Ph-3′–H, d, 2H. ^{13}C-NMR ($CDCl_3$, 26 °C), δ_C: 122.818, C–(C=O); 145.185, C–(CMe_2); 124.351, C5;134.025, C6; 127.751, C7; 130.539, C8; 162.489, C(=O); 98.506, Ps-C; 37.499, quat-C; 27.501, Me; 21.940, Me; 162.208, C(=O, phenyl); 134.977, C*ipso*; 130.981, C2′; 123.670, C3′; 159.916, C4′.

3-(*m*-Nitrobenzoyloxy)-4,4-dimethyl-3,4-dihydro-[1H]-isobenzopyran-1-one, 18

The product with R_f 0.83 (SiO_2, $CHCl_3$:EtOAc; 10:1) was compound **18**, an oil. ^{1}H-NMR ($CDCl_3$, 26 °C), δ_H: 7.470, Ar–H_8, d, 1H; 7.489, Ar–H_7, t, 1H; 7.624, t, Ar–H_6, t, 1H; 8.403, Ar–H_5, d, 1H; 1.517, methyls, s, 6H; 6.682, Ps–H, s, 1H; 8.645, PhC2′, s; 8.165, PhC4′, d, 1H; 7.725, PhC5′, t, 1H; 8.147, PhC6′, d, 1H. ^{13}C-NMR ($CDCl_3$, 26 °C), δ_C: 122.794, C–(C=O); 145.177, C-(CMe_2);124.785, C5; 135.016, C6; 127.759, C7; 129.912, C8; 162.526, C(=O); 98.498, Ps-C; 37.515, quat-C; 27.346, Me; 21.963, Me; 162.255, C(=O, phenyl); 130.501, PhC*ipso*; 124.382, PhC2′; 148.267, PhC3′; 127.759, PhC4′; 128.138, PhC5′; 135.318, PhC6′.

(1[3H]-Isobenzofuranone-3-yl)(4,4,dimethyl-3,4-dihydro-[1H]-isobenzopyran-1-one-3-yl)ether, 19

To a solution of *o*-formylbenzoic acid (**1**, 75 mg, 0.50 mmol) and 3-hydreoxy-4,4-dimethyl-3,4-dihydroisobenzopyran-1-one (**4**, 96 mg, 0.50 mmol) in 5.0 mL CH_2Cl_2, 103 mg

Table 2 Crystallographic information on normal-pseudo anhydride structures **11**, **12**, **17**

Compound	**11**	**12**	**17**
Formula	$C_{15}H_{10}O_4$	$C_{16}H_{12}O_4$	$C_{18}H_{15}NO_6$
FW	254.24	268.27	341.32
Temp. (K)	297	297	101
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	P $2_1/c$	P *bca*	P − 1
a (Å)	13.7593(4)	7.6616(4)	8.5727(6)
b (Å)	7.6299(2)	10.8625(5)	8.7135(6)
c (Å)	11.8981(5)	31.0942(12)	11.0926(6)
α (°)	90	90	76.685(5)
β (°)	92.215(3)	90	75.424(5)
γ (°)	90	90	85.131(6)
Volume (Å^3)	1248.15(7)	2587.8(2)	780.0(9)
Z	4	8	2
F_{000}	528	1120	356
d_{calc} (Mg/m^3)	1.353	1.377	1.453
Unique refl., $I > 4\sigma_I$	4091 2597	1988 1584	5020 4374
Parameters, restraints	172, 0	182, 0	226, 0
R_1 ($I > 4\sigma_I$)	0.0544	0.0329	0.0365
wR_2(all)	0.1186	0.0876	0.1036
GooF	1.012	1.028	1.030
$\Delta\rho_{max,\ min}$ (e$^-$/Å^3)	+0.27 −0.14	+0.11 −0.14	+0.43 −0.23

Estimated standard deviations in parentheses

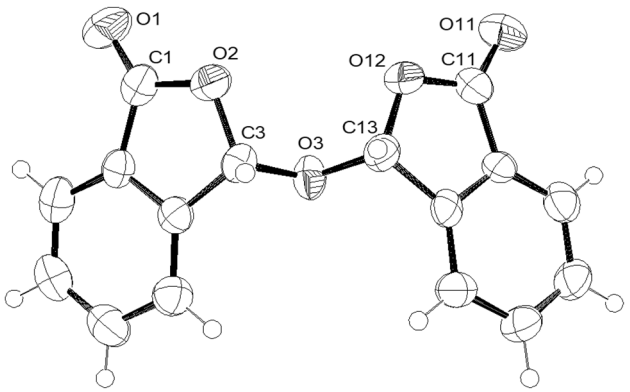


Fig. 1 Thermal ellipsoid plot (50% envelopes) of the molecular structure of **6** (*meso*) showing the approximate mirror

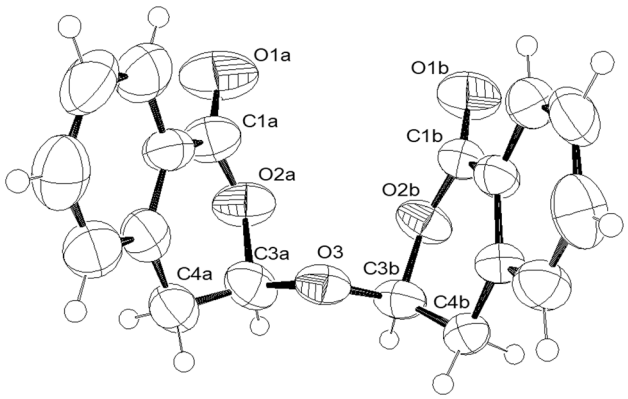


Fig. 2 Thermal ellipsoid plot (50% envelopes) of the molecular structure of **9** (*meso*) showing the approximate mirror

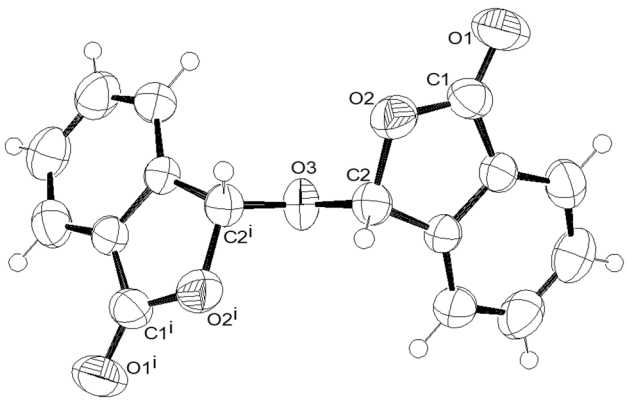


Fig. 3 Thermal ellipsoid plot (50% envelopes) of the molecular structure of **5a** shown down the two-fold axis

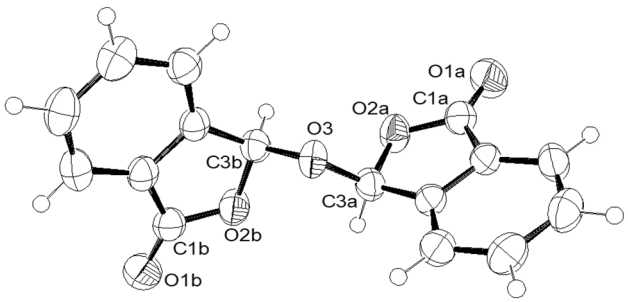


Fig. 4 Thermal ellipsoid plot (50% envelopes) of the molecular structure of **5b** shown down the approximate two-fold axis

(0.50 mmol) DCCI was added and stirred at 0 °C until the reactants were in solution. Then, a catalytic amount of DMAP was added. The mixture stood for 48 h at − 10 °C, then warmed to room temperature, and tlc [silica; $CHCl_3$:ethyl acetate (10:1)] showed bands at R_f 0.85 (major), 0.75 (major), 0.60 (minor). Dicyclohexylurea was filtered and the dichloromethane solution was concentrated. The oily mixture was separated by thick-layer chromatography [silica, $CHCl_3$:ethyl acetate (10:1)]. The R_f 0.85 band was the isophthalide of **4**; the R_f 0.6 band was the active ester of **1**, each determined by nmr. The R_f 0.75 band by nmr showed about 30% of the symmetric dipseudoanhydride **5** (*RR*/*SS*) or **6** (*meso*), and 70% of a second anhydride with pseudoacyl

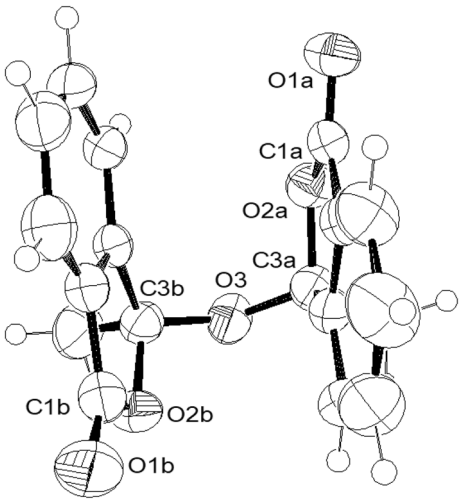


Fig. 5 Thermal ellipsoid plot (50% envelopes) of the molecular structure of **8** shown nearly down the approximate two-fold axis

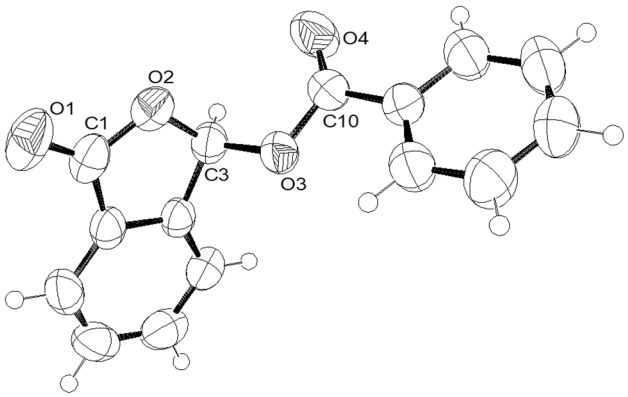


Fig. 6 Thermal ellipsoid plot (50% envelopes) of the molecular structure of **11**

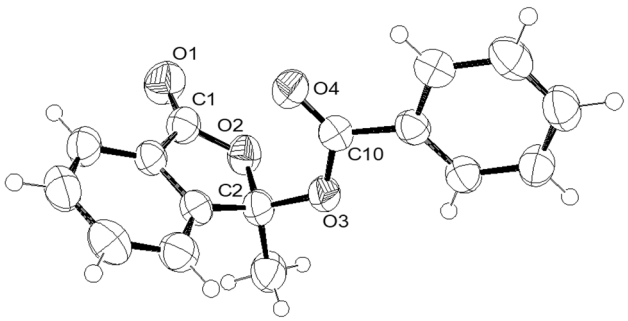


Fig. 7 Thermal ellipsoid plot (50% envelopes) of the molecular structure of **12**

signals for both an arylfuran and an arylpyran group. On fractional crystallization from ethyl acetate, the (*R,R*/*S,S*) form (**5a**) crystallized first, followed by the unsymmetric dipseudoanhydride **19**. For **19:** IR: 1778 cm^{-1} (νC=O furanone), 1733 cm^{-1} (νC=O, pyranone); ^{1}H-NMR ($CDCl_3$, 25 °C), δ_H: (6-ring) 8.1, d, 1H, ar–H nearest C=O; 7.7, t, 1H; 7.6, t, 1H; 7.4, d, 1H; 5.65, s, 1H, Ps–H; 1.41, s, 3H, Me; 1.48, s, 3H, Me; (5-ring) 7.8, d, 1H, ar–H nearest C=O; 7.6, t, 1H; 7.4, t, 1H; 7.6, d, 1H; 6.8, s, 1H, Ps–H; ^{13}C-NMR ($CDCl_3$, 25 °C), δ_C: 168.08; (5-ring)C=O; 163.26; (6-ring) C=O; benzopyran: 123.73, C–(C=O); 145.93, C(CMe_2), 124.69, C3; 131.38, C4; 127.40, C5; 130.23, C6; 104.85, Ps-C; 37.1, quat-C; 27.0, 22.0 Me's; benzofuran: 144.29, 134.86, 134.68, 126.57, 125.52, 123.07, ar–C's; 98.4, benzofuran Ps-C;

Crystallography

Specimens suitable for single-crystal diffraction experiments were mounted with epoxy atop a fine glass fiber for room temperature data collection, or adhered to a fine nylon loop with fluorocarbon oil for low temperature data collection. A Rigaku Gemini diffractometer with a CCD camera was used for **5a**, **5b**, **11**, **12**, **17** and **19**, and a Nicolet-Bruker P3 diffractometer with a scintillation counter were used for **6**, **8**, and **9**. Data for the diffraction experiments is given for the dipseudoanhydrides in Table 1 and for the normal-pseudo anhydrides in Table 2. Structures were solved with SHELXS-86 and refined by full-matrix least-squares methods with SHELXL-97 [17]. Non-H atoms were refined with anisotropic librational factors; H-atoms were assigned positions riding on their non-H atoms with isotropic librational factors of 120% or 150% (methyls) of the U_{eq} of the non-H atoms. Absorption corrections were applied. Thermal ellipsoid plots of each of the structures are given in Figs. 1, 2, 3, 4, 5, 6, 7, 8 and 9. Selected bonding metrics are given in Table 3.

Crystals of the (*R,R*/*S,S*) diastereomer **5** apparently form three polymorphs, monoclinic **5a**, orthorhombic **5b**, and a monoclinic structure previously reported [2]. For **5a**, twinned, non-merohedral, pseudo cell was approximately hexagonal, $a = b = 8.034$ Å, $c = 57.2$ Å, $\gamma = 119.1^{o}$, but exactly orthorhombic, C-centered with $a = 13.8$ Å, $b = 8.14$ Å, $c = 57.27$ Å. In the specimens examined, perfect twinning on the *a*-axis of a C-centered monoclinic cell was found (see Table 2) and the two twin components had almost exactly the same domain size, with 2485 reflections observed in one component, and 2490 reflections in the second, and 770 perfectly overlapped. Twin refinement was satisfactory and the scale factor for the major component was 0.511(1).

Crystals of **6**, the *meso* isomer, were typically affected by non-crystallographic translational symmetry along the *n*-glide. The specimen reported here was largely free of this challenge. This structure has also been reported, and the two determinations agree closely [18].

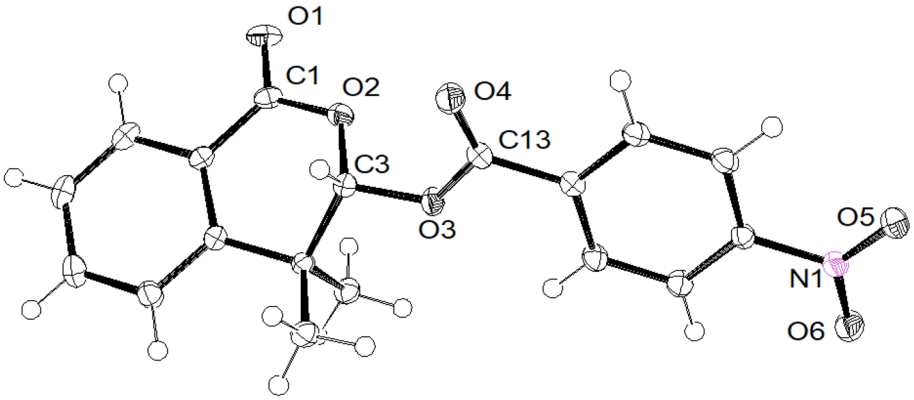


Fig. 8 Thermal ellipsoid plot (50% envelopes) of the molecular structure of **17**

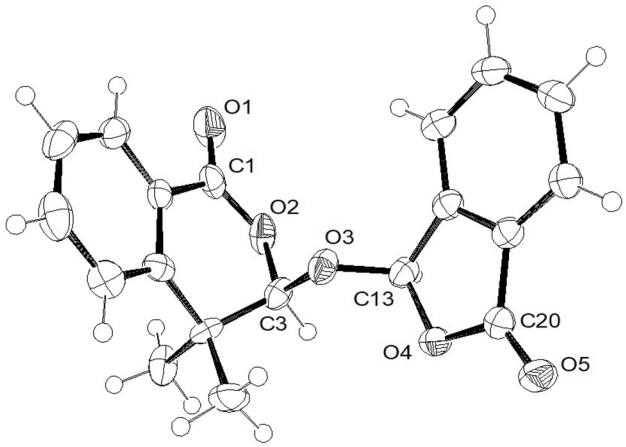


Fig. 9 Thermal ellipsoid plot (50% envelopes) of the molecular structure of the unsymmetric dipseudoanhydride **19**

Crystals of **7** were obtained by sublimation, colorless rods, monoclinic, space group C *c*, $a = 7.916(7)$ Å, $b = 13.396(13)$ Å, $c = 13.620(16)$ Å, $\beta = 96.13(8)$, $V = 1436(3)$ Å^3, $Z = 8$ (2 molecules/asymmetric unit), 293 K, Mo Kα, $C_9H_6O_2$, $M_r = 292.28$ g/mol [19].

A second phase of 3-chloro-1[3H]-isobenzofuranone, $C_8H_5ClO_2$, was included in the analysis of bond metrics. This phase was reported previously, monoclinic, space group P $2_1/c$, $a = 12.938(7)$ Å, $b = 8.027(4)$ Å, $c = 7.184(4)$ Å, $\beta = 94.87(4)^o$, $V = 743.4(7)$ Å^3, $Z = 4$ [19]. In this structure: n C–O is 1.409(3)Å; angle O_n-C–Cl is 108.7(2)^o. It was a polymorph of another phase reported earlier, orthorhombic, space group P *bca*, $V = 1475.2(12)$ Å^3, $Z = 8$ [2].

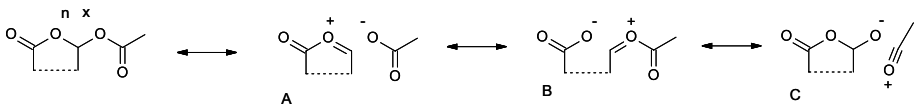
Crystals of the unsymmetric dipseudoanhydride, **19**, form a conglomerate, and the specimen studied was of the *R,R'* diastereomer; Flack 0.07(14). The arylfuran moiety was ordered but the arylpyran moiety was modeled with two

Table 3 Carbon-oxygen bond metrics in anhydrides [P = pseudoacyl; N = normal carboxyl; x = exocylic; n = endocyclic; estimated standard deviations in parentheses]

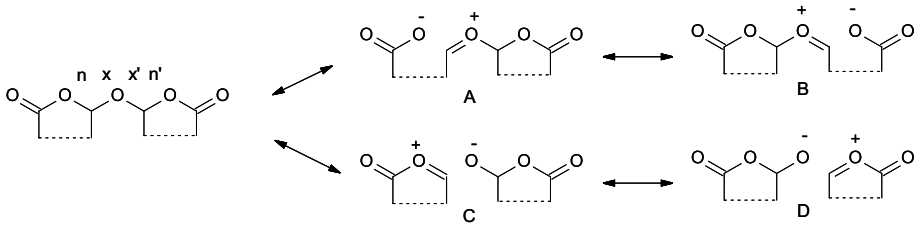
Compound	**5a**	**5b**	**6**	**8**	**9**	**19**	**11**	**12**	**17**
Ps C=O	1.202(1)	1.199(3)	1.191(5)	1.200(3)	1.192(5)	1.196(2)	1.194(2)	1.194(2)	1.212(1)
Ps=C–O	1.369(1)	1.366(3)	1.371(6)	1.370(3)	1.346(6)	1.374(2)	1.364(2)	1.371(2)	1.355(1)
Ps n C–O	1.443(1)	1.440(2)	1.449(6)	1.461(2)	1.462(5)	1.444(2)	1.430(2)	1.442(2)	1.442(1)
Ps x C–O	1.404(1)	1.404(2)	1.397(5)	1.407(2)	1.438(4)	1.407(2)	1.417(2)	1.434(2)	1.415(1)
Ps' x C–O	1.404(1)	1.411(2)	1.416(5)	1.416(2)	1.447(4)	1.418(3)			
Ps' n C–O	1.443(1)	1.436(3)	1.437(6)	1.461(2)	1.455(5)	1.435(5)			
Ps'=C–O	1.369(1)	1.368(3)	1.386(7)	1.358(2)	1.362(5)	1.375(5)			
Ps' C=O	1.202(1)	1.199(3)	1.190(6)	1.197(2)	1.196(5)	1.208(3)			
N O–C=							1.374(2)	1.359(2)	1.358(1)
N C=O							1.190(2)	1.201(2)	1.201(1)
τ OC*O*C[a]	−87.0(1)	−67.2(2)	−98.7(5)	−80.8(2)	−84.7(4)	−99.8(3)	−86.6(2)	+60.7(2)	+84.6(1)
Conform.	−87.0(1) (5)*exo*	−61.8(2) (5)*exo*	+85.1(5) (5)*exo*	−80.3(2) (5)*endo*	+82.7(4) (6)*axial exo*	−92.3(4) *(5)exo (6)axial exo*	(5)*exo*	(5)*endo*	(6)*equat.*
Config.	*R,R/S,S*	*R,R/S,S*	*meso*	*R,R/S,S*	*meso*	*R,R'*	Racemate	Racemate	Racemate

[a]Torsion angles for a common relative configuration; (5) refers to arylfuran and (6) to arylpyran rings. For **19**, arylfuran entries precede arylpyran entries; metrics for the major conformer

Scheme 2 Resonance structures for normal-pseudo anhydrides



Scheme 3 Resonance structures for dipseudoanhydrides



contributors, major component 0.645(8), differing in conformation about the *exo* C_5–O_5–O_{ether}–C_6 torsion, −99.8(3)° (major), −87.5(4)° (minor).

Discussion

Chemistry

A variety of methods for forming pseudoanhydrides has been explored and found to be useful. Effective methods beyond thermal dehydration have been demonstrated, each involving (putatively) reactive intermediates. The displacement of a pseudochloride by a nucleophilic oxygen seems the more likely mechanism for formation of **9** and perhaps the formation of a pseudoester of *o*-benzoylbenzoyl chloride by sodium benzoate [2]. The new methods demonstrated here involve the dicyclohexylcarbodiimide coupling reaction. Formation of the active esters of normal carboxylic acids is a well known first step in acyl substitution, and it is shown here that pseudoacids (**1**, **2**, **4**) are able to displace the activating group and form the anhydrides. Pseudoacyl oxygens are expected to be better nucleophiles than carboxylic acid oxygens, so this is not unanticiptated. The reaction to form the dipseudoanhydride **19**, however, provides tentative evidence of another mechanism. Relatively unhindered pseudoacids (those from aldehydo acids) may apparently form pseudoacyl active esters, which can be displaced by a pseudoacid. Intermediate pseudoacyl active esters have not been observed yet, so this mechanism will require more evidence.

Structures

Normal-pseudo anhydrides (**11**, **12**, **17**). In each of these structures, the pseudoacyl carbon bears competing exocyclic and endocyclic carboxylate groups. In the examples **11** and **12** (Fig. 6 and 7), the cyclic form is an arylfuran ring and the carboxylates are (substituted) benzoates. With similar basicities (about pKa ~ 5), we might expect roughly equal

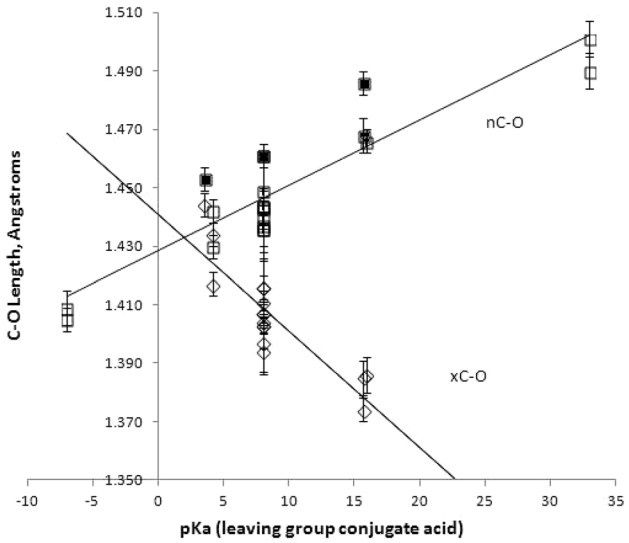


Fig. 10 C–O Bond Lengths at the Pseudoacyl Carbons in Arylfuran Pseudoacyl Derivatives of *o*-Acylbenzoic Acids, estimated standard deviations (x 2); outliers with filled markers (see text)

contributions to the ground state from resonance contributors A and B (Scheme 2). A test for this hypothesis may be found comparing pseudoacyl C–O lengths, where the exocyclic C–O bonds (x) and the endocyclic C–O bonds (n) should have similar lengths. In both structures, n C–O is longer than x C–O for these normal-pseudo anhydrides (n 1.441Å, x 1.416Å, difference 0.025Å, N = 3, Table 2). This result implies that the endocyclic carboxylate is the better leaving group, and that the endocyclic carboxyl (part of the pseudoacid) is the stronger acid. For normal-pseudo anhydrides, contributions to the ground state structure from resonance forms like B (Scheme 2) are important.

It has been observed preciously that at pK_a 2.4 for the (conjugate acid of the) exocyclic group would show equal n C–O and x C–O lengths in an arylfuran pseudoacyl system [2]. The C–O data from the arylpyran system (**17**) is similar to the furans, and this example is included in the set though

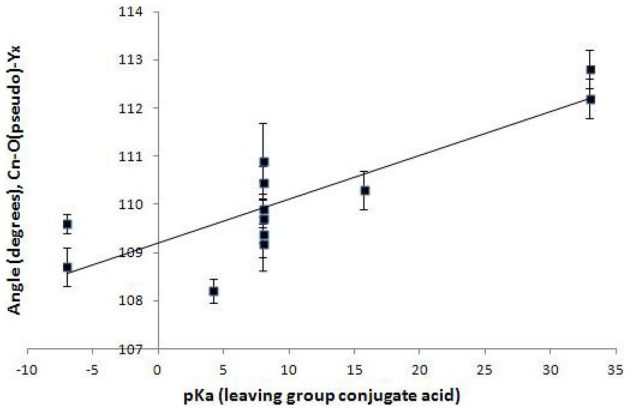


Fig. 11 O_n–C–Y_x Bond Angles at the Pseudoacyl Carbons for Arylfuran Pseudoacyl Derivatives of *o*-Formylbenzoic Acid, estimated standard deviations (×2); see text

the C–O bond length dependency on leaving group ability has not been established for the arylpyrans yet. The effective enhanced acidity of the endocyclic (pseudo)carboxyl is tentatively supported and estimated to be about 3 pK units stronger relative to a nominal carboxylic acid.

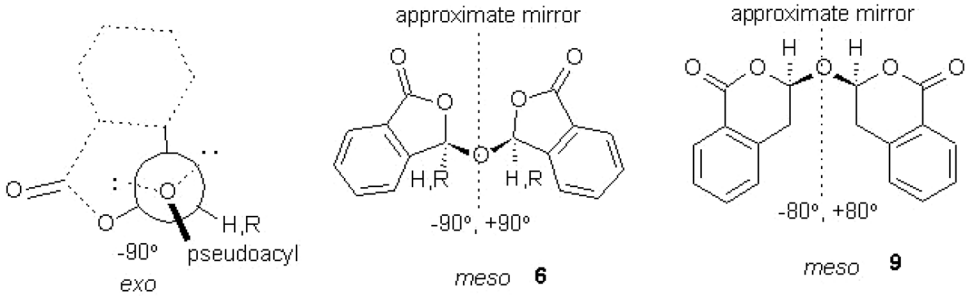
Dipseudoanhydrides

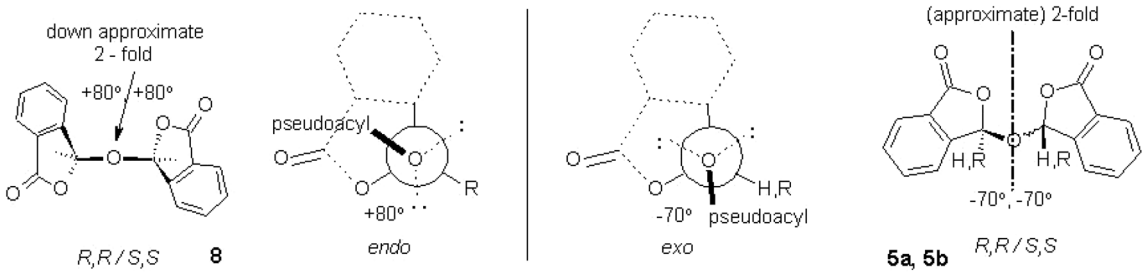
Five of the six dipseudoanhydrides studied are symmetrical (either *meso* or racemate of *R,R/S,S* isomers) (Figs. 1, 2, 3, 4, 5). Only in crystals of **5a** (an RR/SS form) does the crystal lattice use the molecular symmetry with the ether oxygen lying on the crystallographic twofold axis in C 2/*c*, making half-molecules the asymmetric unit. In the others (**5b**, **6**, **8**, **9**) and in a sixth (**19**, an unsymmetrical anhydride between pseudoacids **1** and **4**) molecules occupy general positions. The dipseudoanhydrides (**5**, **6**, **8**, **9, 19**) studied comprise both arylfuran and arylpyran examples. These structures present competing pseudocarboxyl (C, D, Scheme 3) or carboxyl leaving groups (A, B, Scheme 3), a disparity between n C–O and x C–O is still expected, since carboxylate is a better leaving group than pseudocarboxylate. If structures like A, B are more important than C, D (Scheme 3), then n C–O would be longer than x C–O. All dipseudoanhydride structures show this disparity (n 1.449Å, x 1.407Å; difference 0.042Å, N = 14), and this difference is slightly larger than in the normal-pseudo anhydrides (*vide supra*).

With the addition of the arylfuran pseudoacyl derivative data from **5a, 5b**, **6**, **8**, **11**, **12**, and **19** to the limited information in the literature, the C–O bond length functions for the arylfuran system can be reconstructed [2, 18–20]. Figure 10 shows the C–O bond length trends at the pseudoacyl carbon for cyclic *o*-acylbenzoic acid derivatives. The range of pK_a's (conjugate acid of the implied leaving groups) is now extended to include the pseudoacyl chlorides. A pK_a of 8 is used for the treatment of the pseudoacyl leaving group [2]. Trends are reasonably well established, with the n C–O function (in Å) = 1.4287 + 0.0022322 pKa (N = 20, R^2 = 0.83), and x C–O (in Å) = 1.4408 − 0.0039882 pKa (N = 16, R^2 = 0.75). In the previous determination, which excluded the pseudoacyl chlorides, the n C–O slope was smaller and the x C–O slope was larger [2]. The crossover length, the distance at which endocyclic and exocyclic C–O's are equal, is 1.433 Å at a pK_a of 1.94. Since this is about 3 pK units more acidic than normal carboxylic acids, this represents the effective increase in the endocyclic leaving group ability owing to ring formation. A model for this is captured in resonance structures A, B (Scheme 3).

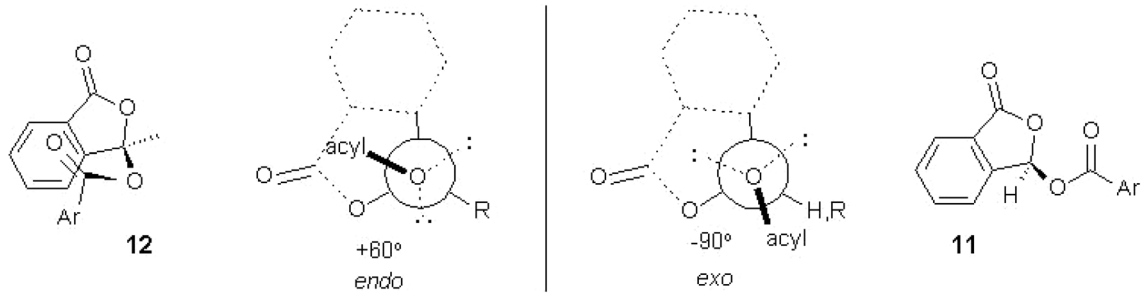
Clues to the source of this effect may be found by examination of the arylfurans from *o*-formylbenzoic acid including five (**5a**, **5b**, **6**, **11**, **19**) reported here. Structures for these span the range of leaving group pK_a explored above. Figure 11 shows the O_n–C–X angles at the pseudoacyl carbon (all *exo* conformers, see below and Table 2), for which a trend is evident while the correlation is modest (R^2 = 0.71). The longer n C–O's show angles of departure (~ 112°) of the endocyclic leaving group above the Bürgi-Dunitz angle (107°) [21]. This suggests that the interaction of the endocyclic nucleophile in ring formation may approach along a non-optimal trajectory, for which a stronger endocyclic Lewis-basicity or a weaker leaving group Lewis-basicity are partial remedies. The changing polarization (partial ionic character) of the C–O bonds follow different dependencies (slopes of the two C–O functions differ by about a factor of 2) with the endocyclic function more restricted. Even with

Scheme 4 Drawing of arylfuran and arylpyran conformations looking down the pseudoacyl C–O_{ether} bond. Orientation of the exocyclic O_{ether}–$C_{pseudoacyl}$ group is shown with a darkened bond





Scheme 5 Drawing of arylfuran conformations looking down the pseudoacyl C–O_{ether} bond. Orientation of the endo- and exocyclic O_{ether}–$C_{pseudoacyl}$ group is shown with a darkened bond



Scheme 6 Drawing of arylfuran conformations looking down the pseudoacyl C–O_{ether} bond. Orientation of the endo- and exocyclic O_{ether}–C_{acyl} group is shown with a darkened bond

better leaving groups (lower conjugate acid pKa), the endocyclic angle of approach is still above 107°.

This analysis focused on arylfurans, and Fig. 10 omits the benzopyranoid structures. Similar length disparities (n C–O > x C–O) are observed in the arylpyrans for the dipseudo anhydride **9,** normal, pseudo anhydride, **17**, and unsymmetric dipseudo anhydride **19** (Table 3). Also, in the diastereomereic pairs of mucochloric psedoanhydrides, a furanoid system, n C–Os are longer than x C–Os (n 1.430Å, x 1.398Å, difference 0.032Å, N = 4) [7]. From Fig. 10, it is clear that the n C–O lengths in the normal-pseudo anhydride of *o*-benzoylbenzoic acid (pK_a 3.54), its psueudo methyl ester (pK_a 15.9), dipseudoanhydride **8** (pK_a 8), and for pseudoacid *o*-acetylbenzoic acid (pK_a 15.7) are modest positive outliers [2, 20]. These are compounds with four non-H atoms including aryl and alkyl substitutions on the pseudoacyl carbon, and their C–O bonds are systematically slightly lengthened by steric effects [22]. A narrowed analysis of only the cyclic derivatives of *o*-formybenzoic acid, which form the majority of the study group, does not alter the slopes appreciably, with the crossover C–O distance reduced to 1.428 Å at a pK_a of 1.81. For this set, n C–O (in Å) = 1.4242 + 0.0022211 pK_a (N = 15, R^2 = 0.96), and for x C–O (in Å) = 1.4346 − 0.035136 pKa (N = 11, R^2 = 0.63).

Conformations

Of the five symmetric dipseudoanhydrides structures studied (**5a**, **5b**, **6**, **8**, **9**) two are *meso* and three are (*R,R/S,S*) forms. The ring systems are fairly rigid groups. For both benzofuran and benzopyran systems, linking (ether) oxygens are displaced from the mean ring planes. Orientations of the rings with respect to each other can be described by the O(ring)–C(pseudo)–O(ether)–C(pseudo′) torsions which are typically *gauche* and *synclinal* to the ring C–O and substituents are either *exo* (oriented away from the rings) or *endo* (oriented over the ring). Scheme 4 shows the conformations down the C(pseudo)-O(ether) bonds for *meso* forms with *exo* conformations. Torsion angles relevant to the conformations are given in Table 2. Molecules in **6** and **9** occupy general positions, and the mirror symmetry of the *meso* forms are not displayed in the crystal.

Dipseudoanhydrides with (*R,R/S,S)* configurations show both *endo* and *exo* conformations (Scheme 5). Compound **5a** retains is molecular two-fold in the crystal while **5b** and **8** occupy general positions and molecules show approximate two-fold symmetry.

The arylpyran anhydride moiety of **9** has an *axial* (α-anomer) conformation additionally (see Scheme 4). In unsymmetric anhydride **19**, the arylpyran part has an *axial* conformation and the pseudoacyl attachment is *exo*. For the

arylfuran part of **19**, its pseudoacyl substituent also has an *exo* conformation. Arylfuran normal-pseudo anhydrides **11** and **12** are racemates, and these show both *endo* and *exo* conformations (Scheme 6). As noted above, arylpyrans in **9** and **19** are in *axial* conformations while in **17**, the pseudoacyl nitrobenzoyloxy group is *equatorial* (β-anomer).

Supplementary Materials Available

Crystallographic information for (**5a**: 1913208; **5b**: 1913205; **6**: 1913211; **8**: 1913212; **9**: 1913207; **11**: 1913209; **12**: 1913206; **17**: 1913210; **19**: 1915554) have been deposited with the Cambridge Crystallographic Data Center. Structural data can be obtained 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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