Facile Synthesis of Carboxylic Anhydrides Using 4,5-Dichloro-2-[(4-nitrophenyl)sulfonyl]pyridazin-3(2*H*)-one

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Abstract: A novel and facile synthesis of carboxylic anhydrides from carboxylic acid using 4,5-dichloro-2-[(4-nitrophenyl)sulfonyl]pyridazin-3(2*H*)-one (**2**) is presented. Treatment of aliphatic or aromatic carboxylic acids with **2** in the presence of base in organic solvents gave the corresponding anhydrides in good or excellent yields

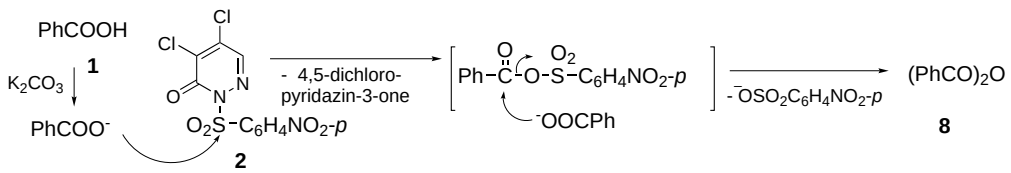
Key words: 4,5-dichloro-2-[4-nitrophenyl)sulfonyl]pyridazin-3(2*H*)-one, carboxylic anhydride, sulfonyl-transfer

Carboxylic anhydrides are useful compounds either as acylating agents or as intermediates in organic synthesis, because of the enhanced electrophilic character of the carbonyl goups.[1] The availability of symmetric acid anhydrides is quite important for many transacylation applications,[2] because they do not give any by-products due to attack at the second acyl carbonyl group, which is the case when mixed anhydrides are used. Carboxylic acid anhydrides are usually prepared by reacting carboxylic acids with dehydrative coupling agents such as thionyl chloride,[2,3] phosgene,[4] phosphorus pentoxide,[5] isocyanate,[6] 1,3-dicyclohexylcarbodiimide[7] or ethoxyacetylene, [1g,1h,8] or reacting carboxylate salts with powerful acylating agents such as acid chloride[9] or acid anhydrides.[10] These reagents have some drawbacks that limit their application: instability, toxicity, insolubility and high volatility. In order to overcome the problems, some *N*-sulfonylheterocycles such as 1-(mesitylenesulfonyl)-3-nitro-1,2,4-triazole,[11] 3-nitro-1-[(2,4,6-triisopropylphenyl)sulfonyl]-1,2,4-triazole[12] and 1-[methane(or phenyl)sulfonyl]-benzotriazole[13a] have been developed as mild and stable electrophilic sulfonyl group transfer reagents. These *N*-sulfonylheterocycles convert carboxylic acids into their corresponding anhydrides via sulfonylcarboxylates (RCO_2SO_2R) as key intermediates.[13]

In continuation of our studies on the reactivity and application of 2-(arylsulfonyl)pyridazin-3(2*H*)-ones, we found that benzenesulfonyl group of 4,5-dichloro-2-(arylsulfonyl)pyridazin-3(2*H*)-ones transferred to some aliphatic amines[14] and that the treatment of 2-(phenylsulfonyl)pyridazin-3(2*H*)-ones with carboxylic acid in the presence of a base formed the corresponding sulfonylcarboxylates (RCO_2SO_2R). Moreover, 4,5-dichloropyridazin-3(2*H*)-one is also a stable leaving group.[15] We report here on a mild and facile procedure for synthesizing symmetric acid anhydrides from carboxylic acids using 4,5-dichloro-2-[(4-nitrophenyl)sulfonyl]pyridazin-3(2*H*)-one (**2**) as a novel mediator.

In order to evaluate the sulfonyl-transfer potentiality of 2-(arylsulfonyl)pyridazin-3(2*H*)-one derivatives, benzoic anhydride (**8**) was synthesized first from benzoic acid (**1**) using some 4,5-dichloro-2-[methane(or arylsulfonyl)]pyridazin-3(2*H*)-ones such as **2**–**7**.[14] The results are shown in Table 1. Benzoic acid (**1**) was treated with compounds **2**–**7** in the presence of K_2CO_3 in THF at 40 °C to give benzoic anhydride (**8**) in 56–97% yields. The proposed mechanism is shown in Scheme 1.

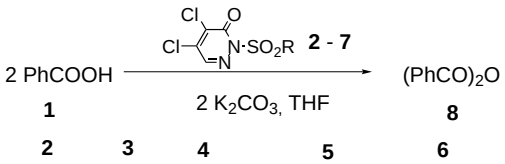
Compound **2** showed the best results. To compare the sulfonyl-transfer potentiality of **2** with other *N*-[(4-nitrophenyl)sulfonyl]heterocycles, we also attempted to synthesize benzoic anhydride (**8**) from benzoic acid (**1**) using compounds **9**,[13a] **10**[16] and **11**.[16] Treatment of acid **1** with **9** in the presence of K_2CO_3 in THF gave 1-benzoylbenzotriazole (**12**) instead of anhydride in 92% yield (Table 2). During the reaction of **1** with **9**, we could not detect the formation of the corresponding anhydride by TLC monitoring. This result may be due to the fact that the reaction rate of benzotriazole anion for sulfonylcarboxylate is faster than that of the carboxylate ion. Katritzky and his co-workers[13a] had also reported a similar result.



Scheme 1

Synthesis 2003, No. 10, Print: 21 07 2003.
Art Id.1437-210X,E;2003,0,10,1517,1520,ftx,en;F02403SS.pdf.

Table 1 Synthesis of Benzoic Anhydride (**8**) using *N*-Sulfonylpyridazinones **2**–**7** in the Presence of K_2CO_3 in THF at 40 °C

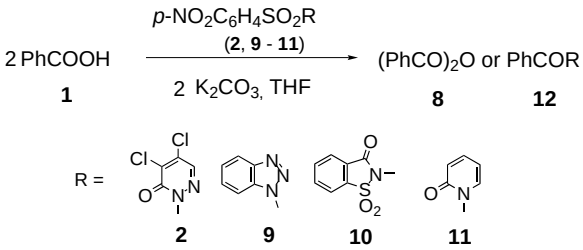


R	2 $C_6H_4NO_2$-*p*	3 Ph	4 C_6H_4Me-*p*	5 C_6H_4CN-*o*	6 $C_6H_4NO_2$-*o*	7 Me

Entry	*N*-Sulfonylpyridazinone	Time (h)	Anhydride **8** (%)[a]	Pyridazinone[c] (%)
1	**2**	3	97	96
2	**3**	96	89	90
3	**4**	216	95	93
4	**5**	6	93	94
5	**6**	4	56[b]	48
6	**7**	3	86	88

[a] Isolated yield.
[b] The unreacted starting material was recovered.
[c] 4,5-Dichloropyridazin-3(2*H*)-one.

Table 2 Reaction of Benzoic Acid (**1**) with some *N*-Sulfonylheterocycles **2** and **9**–**11** in the Presence of K_2CO_3 in THF at 40 °C



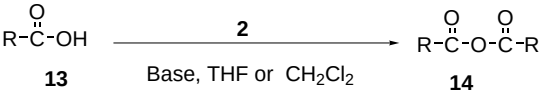
Entry	*N*-Sulfonylheterocycle	Time (h)	Product (%)[a]	
			Anhydride	Amide
1	**2**	3	**8** (97)	–
2	**9**	57	–	**12** (92)
3	**10**	190	**8** (30)[b]	–
4	**11**	–	no reaction	–

[a] Isolated yield.
[b] The unreacted starting material was recovered.

Reaction of acid **1** with **10** under the given conditions for 190 hours gave anhydride **8** in 30% yield. Reaction of acid **1** with **11** , however, did not proceed. Compared to the reactivity of four *N*-[(4-nitrophenyl)sulfonyl]heterocycles for the synthesis of benzoic anhydride (**8**), compound **2** is definitely superior to the others under our conditions. Therefore, we selected compound **2** as a novel mediator for the direct synthesis of anhydrides from carboxylic acids.

Treatment of aliphatic or aromatic carboxylic acids **13** (2 equiv) with compound **2** (1 equiv) in the presence of base (2 equiv) such as K_2CO_3, 4-(*N*,*N*-dimethylamino)pyridine for **13f** and triethylamine for **13a** and **13c** in THF or CH_2Cl_2 at 40 °C easily gave the corresponding anhydrides **14** in 70–98% yields (Table 3). Use of triethylamine or 4-(*N*,*N*-dimethylamino)pyridine, respectively, as a base for the preparation of **14a** and **14c**, and **14f** is more favorable than K_2CO_3 with respect to improvement of yields. The other products, 4,5-dichloropyridazin-3(2*H*)-one and 4-nitrobenzenesulfonate salt, were isolated in excellent or good yields (Table 3).

Table 3 Yields and Conditions for the Synthesis of Anhydrides from Carboxylic Acids Using **2**



Entry	RCO_2H R		Base[a]	Time (h)	Method (%)[b]	Anhydride	Yield
1	**13a**	$CH_3(CH_2)_{14}$	Et_3N	18	B	**14a**	86
2	**13b**	Me_2C=CH	K_2CO_3	3	B	**14b**	92
3	**13c**	(*E*)-PhCH=CH	Et_3N	5	A	**14c**	72
4	**13d**	*p*-(*n*-Pr)C_6H_4	K_2CO_3	1.6	C	**14c**	89
5	**13e**	*p*-(CH_2=CH) C_6H_4	K_2CO_3	1.5	B	**14e**	88
6	**13f**	*p*-$MeOC_6H_4$	DMAP	23	C	**14f**	98
7	**13g**	*p*-MeC_6H_4	K_2CO_3	4	B	**14g**	90
8	**13h**	*o*-ClC_6H_4	K_2CO_3	3	B	**14h**	85
9	**13i**	*p*-PhC_6H_4	K_2CO_3	1	C	**14i**	70
10	**13j**	C_8H_5S[c]	K_2CO_3	19	B	**14j**	81

[a] DMAP = 4-(*N*,*N*-dimethylamino)pyridine. Reaction temperature = 40 °C. Two equivalents of base were used. Solvent = CH_2Cl_2 for Entry 1 and 3; THF = Entries 2 and 4–10.
[b] Isolated yield. 4,5-Dichloropyridazin-3(2*H*)-one and 4-nitrobenzenesulfonate salt were also isolated in excellent or good yield.
[c] Thianaphthene-2-yl.

In conclusion, a useful synthesis of symmetric anhydrides was achieved by using 4,5-dichloro-2-[(4-nitrophenyl)sulfonyl]pyridazin-3(2*H*)-one (**2**) as a source of benzenesulfonyl group. This method of preparing anhydrides has the following advantages: i) direct conversion of the acid to anhydride, ii) mild reaction conditions, iii) easy preparation of reagent **2**, iv) use of stable but not hygroscopic solid as a reagent, v) simple experimental procedure, and vi) quantitative recovery of reusable 4,5-dichloropyridazin-3(2*H*)-one and potassium 4-nitrobenzenesulfonate.

Reagents and solvents were used as received from commercial sources. TLC was performed on plates coated with silica gel (silica gel 60 F254, Merck). The spots were located by UV light. Column chromatography was carried out on silica gel (silica gel 60, 70–230 mesh). Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were

obtained on a Bruker FT NMR-DRX 500 or Varian Inova 500 spectrometer. The chemical shift values are reported in δ units (part per million) relative to TMS as an internal standard. IR spectra were obtained on a Hitachi 270-50 or Mattson Genesis Series FT-IR spectrophotometer. Elemental analyses were performed with a Perkin-Elmer 240C. Mass spectra were recorded with a Jeol JMS-700 spectrometer.

Carboxylic Anhydrides 8 and 14a–j; General Procedures

Method A: A mixture of carboxylic acid **1** or **13** (3.13 mmol, 2 equiv), base (2 equiv) and **2** (1.565 mmol, 1 equiv) in anhyd THF (30 mL) was refluxed until **2** had disappeared (TLC monitoring). After cooling to r.t, the mixture was filtered and washed with THF (50 mL). After evaporating the combined filtrate under reduced pressure, the anhydride was extracted with *n*-hexane (180 mL) from the resulting residue. The hexane solution was evaporated under reduced pressure to give the corresponding anhydrides in good or excellent yields. 4,5-Dichloropyridazin-3(2*H*)-one was recovered from the residue in quantitative yield by filtration and washing with H_2O (100 mL). The aqueous filtrate was evaporated under reduced pressure. After triturating the residue with THF (70 mL), the solid was filtered and dried in air to give potassium 4-nitrobenzenesulfonate in good yield. The obtained 4,5-dichloropyridazin-3(2*H*)-one and potassium 4-nitrobenzenesulfonate were identical with authentic compounds.

Method B: A mixture of carboxylic acid **1** or **13** (3.13 mmol, 2 equiv), base (2 equiv) and **2** (1.565 mmol, 1 equiv) in anhyd THF (30 mL) was refluxed until **2** had disappeared (TLC monitoring). After cooling to r.t., the mixture was filtered. The resulting precipitate was washed with H_2O (100 mL) and the H_2O was evaporated under reduced pressure. After triturating the residue with THF (70 mL), the solid was filtered and dried in air to give potassium 4-nitrobenzenesulfonate in good yield. The combined THF filtrates were also evaporated under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column (3 × 5 cm) and the column was eluted with CH_2Cl_2. Fractions containing anhydride were combined and evaporated under reduced pressure to afford the corresponding anhydrides in good to excellent yields. The fractions containing 4,5-dichloropyridazin-3(2*H*)-one were combined and evaporated under reduced pressure to recover it in quantitative yield.

Method C: A mixture of carboxylic acid **1** or **13** (3.13 mmol, 2 equiv), base (2 equiv) and **2** (1.565 mmol, 1 equiv) in anhyd THF (30 mL) was refluxed until **2** had disappeared (TLC monitoring). After evaporating the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 (200 mL). The mixture was filtered using a sintered glass filter filled silica gel (2 cm). The filtrate was evaporated under reduced pressure to give the corresponding anhydrides in good to excellent yield. After washing the resulting residue with EtOAc (200 mL), the organic filtrates were evaporated under reduced pressure to give 4,5-dichloropyridazin-3(2*H*)-one in quantitative yield. Finally, the residue was washed with H_2O (100 mL), and the aqueous solution was evaporated under reduced pressure. After triturating the residue with THF (50 mL), the soild obtained was filtered and dried in air to give potassium 4-nitrobenzenesulfonate.

Benzoic Anhydride (8)

Mp 40–41 °C (Lit.[17] mp 42 °C).

IR (KBr): 1786 (C=O), 1724 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 7.52 (t, 4 H, *J* = 7.8 Hz), 7.67 (t, 2 H, *J* = 7.5 Hz), 8.16 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 128.8, 128.9, 130.6, 134.5, 162.4.

Palmitic Anhydride (14a)

Mp 63–64 °C (Lit.[19] mp 64 °C).

IR (KBr): 1801 C=O), 1741 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.88 (t, 6 H, *J* = 6.9 Hz), 1.25 (m, 48 H), 1.65 (m, 4 H), 2.44 (t, 4 H, *J* = 7.5 Hz).

^{13}C NMR ($CDCl_3$): δ = 14.1, 22.7, 24.3, 28.9, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9, 35.3, 169.4.

3,3-Dimethylacrylic Anhydride (14b)

Oil.

IR (KBr): 1780 (C=O), 1720 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 1.96 (d, 6 H, *J* = 1.2 Hz), 2.22 (d, 6 H, *J* = 1.2 Hz), 5.71 (q, 2 H, *J* = 1.2 Hz, 1.3 Hz).

^{13}C NMR ($CDCl_3$): δ = 20.8, 27.7, 115.4, 162.1, 162.6.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.94; H, 7.75.

***trans*-Cinnamic Anhydride (14c)**

Mp 136–137 °C (Lit.[20] mp 137–138 °C).

IR (KBr): 1766 (C=O), 1700 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 6.53 (d, 2 H, *J* = 15.9 Hz), 7.42 (m, 6 H), 7.58 (m, 4 H), 7.86 (d, 2 H, *J* = 15.9 Hz).

^{13}C NMR ($CDCl_3$): δ = 116.8, 128.6, 129.1, 131.3, 133.8, 148.7, 162.5.

Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.78; H, 5.09.

***p*-(*n*-Propyl)benzoic Anhydride (14d)**

Oil.

IR (KBr): 1790 (C=O), 1730 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.96 (t, 6 H, *J* = 7.4 Hz), 1.69 (m, 4 H), 2.68 (t, 4 H, *J* = 7.6 Hz), 7.31 (m, 4 H), 8.06 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 13.8, 24.2, 38.2, 126.5, 129.0, 130.7, 150.2, 162.6.

Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.43; H, 7.24.

***p*-Vinylbenzoic Anhydride (14e)**

Mp 59–60 °C.

IR (KBr): 1780 (C=O), 1720 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 5.45 (d, 2 H, *J* = 10.9 Hz), 5.92 (d, 2 H, *J* = 17.6 Hz), 6.78 (m, 2 H), 7.53 (m, 4 H), 8.10 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 117.7, 126.6, 127.9, 130.9, 135.8, 143.6, 162.2.

Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.64; H, 5.09.

***p*-Methoxybenzoic Anhydride (14f)**

Mp 89–90 °C.

IR (KBr): 1790 (C=O), 1720 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.89 (s, 6 H), 6.98 (m, 4 H), 8.09 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 55.6, 114.2, 121.3, 132.8, 162.3, 164.6.

Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 67.22; H, 4.99.

***p*-Methylbenzoic Anhydride (14g)**

Mp 89–90 °C.

IR (KBr): 1772 (C=O), 1710 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 2.48 (s, 6 H), 7.34 (d, 4 H, *J* = 8.01 Hz), 8.06 (d, 4 H, *J* = 8.13 Hz). ^{13}C NMR ($CDCl_3$): δ = 21.9, 126.2, 129.6, 130.6, 145.6, 162.6.

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.61; H, 5.62.

o-Chlorobenzoic Anhydride (14h)
Oil.

IR (KBr): 1790 (C=O), 1735 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 7.49 (m, 2 H), 7.66 (d, 2 H, *J* = 7.96 Hz), 8.03 (d, 2 H, *J* = 7.83 Hz), 8.11 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 128.7, 130.3, 130.4, 130.5, 134.8, 135.3, 160.9.

Anal. Calcd for $C_{14}H_8Cl_2O_3$: C, 56.98; H, 2.73. Found: C, 57.11; H, 2.84.

p-Phenylbenzoic Anhydride (14i)
Mp 138–140 °C.

IR (KBr): 1780 (C=O), 1720 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 7.44 (d, 2 H, *J* = 5.0 Hz), 7.50 (t, 4 H, *J* = 10.0, 5.0 Hz), 7.65 (d, 4 H, *J* = 10.0 Hz), 7.75 (d, 4 H, *J* = 10 Hz), 8.24 (d, 4 H, *J* = 10 Hz).

^{13}C NMR ($CDCl_3$): δ = 127.4, 127.6, 127.7, 128.6, 129.1, 131.2, 139.6, 147.4, 162.4.

Anal. Calcd for $C_{26}H_{18}O_3$: C, 82.52; H, 4.79. Found: C, 82.61; H, 4.87.

Thianaphthene-2-carboxylic Anhydride (14j)
Mp 140–141 °C.

IR (KBr): 1770 (C=O), 1710 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 7.49 (m, 2 H), 7.66 (d, 2 H, *J* = 8.0 Hz), 8.03 (d, 2 H, *J* = 7.8 Hz), 8.11 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 122.9, 125.4, 126.1, 128.1, 131.6, 133.5, 138.5, 143.3, 157.3.

Anal. Calcd for $C_{18}H_{10}S_2O_3$: C, 63.89; H, 2.98; S, 18.95. Found: C, 63.93; H, 3.02; S, 19.01.

1-Benzoylbenzotriazole (12)
This compound was obtained from the reaction of benzoic acid (**1**) with with the *N*-sulfonylheterocycle **9** (Table 2).

Mp 110–111 °C (Lit.[18] mp 112–113 °C).

IR (KBr): 1720 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 7.57 (m, 3 H), 7.69 (m, 2 H), 8.17 (d, 1 H, *J* = 8.3 Hz), 8.22 (d, 2 H, *J* = 7.6 Hz), 8.40 (d, 1 H, *J* = 8.3 Hz).

^{13}C NMR ($CDCl_3$): δ = 114.8, 120.2, 126.4, 128.5, 130.4, 131.6, 131.8, 132.4, 133.7, 145.8, 166.8.

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