Convenient Synthesis of Carboxylic Acid Anhydrides using *N*,*N*-Bis[2-oxo-3-oxazolidinyl]phosphorodiamidic Chloride

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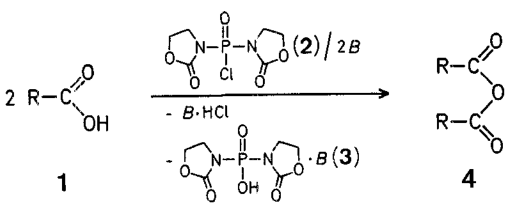
Many methods for the conversion of carboxylic acids into the corresponding acid anhydrides using two-stage, one-flask procedures or one-stage procedures with various reagents have been described[1-4,9-15] and reviewed[5-8]. The yields and the reaction conditions employed vary widely; reaction times from 30 min to 20 h, reaction temperatures from room temperature to reflux in acetic anhydride.

For the preparation of aromatic carboxylic anhydrides, the carbodiimide[1,2] method is frequently employed. However, this method suffers from the disadvantage that the *N*-acylurea is formed as a by-product. In the presence of a tertiary base, the formation of both the anhydride product and the by-product are inhibited. The relative yields depend on the nature of the reagents and the reaction conditions employed[7]; in reactions of triethylammonium salts of the carboxylic acids with dicyclohexylcarbodiimide, only *N*-acylureas are obtained[16].

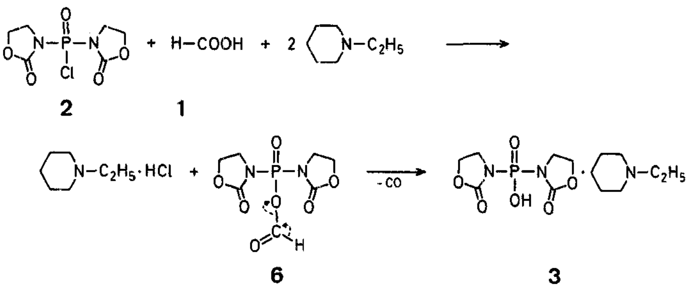
We now report a convenient, one-step synthesis of anhydrides **4** from the tertiary ammonium salts of the carboxylic acids **1** using *N*,*N*-bis[2-oxo-3-oxazolidinyl]phosphorodiamidic chloride[17] {**2**; 3,3'-(chlorodiphosphinylidene)-bis[2-oxo-1,3-oxazolidine]} as shown in Scheme A (see Table 1).



Scheme A

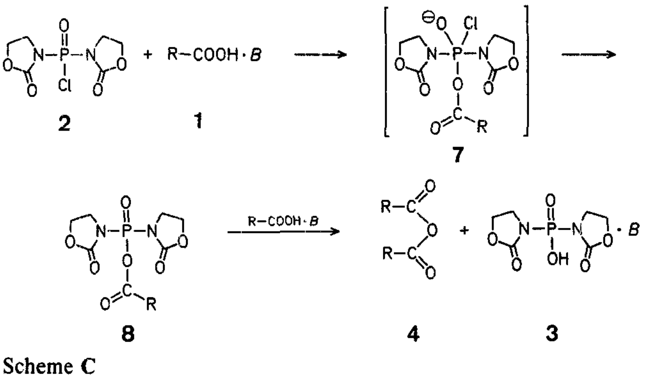
These results are in good accord with our previously described one-step syntheses of amides and esters using the reagent **2**[17].

Reaction of **2** with formic acid (**1**; R = H) results in the quantitative decomposition of the latter at room temperature and thus demonstrates the high activation capacity of the reagent **1** (Scheme **B**).



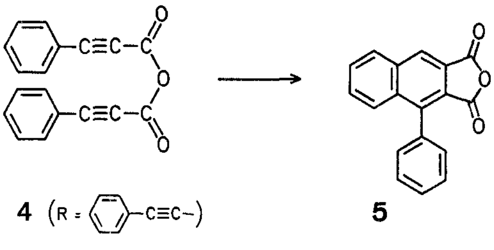
Scheme **B**

In our previous paper[17], we speculated on the possible intermediates on the basis of spectroscopic data. It has since been possible to isolate and characterize the intermediate **8**[18] (Scheme C). In the reactions of tetracoordinate phosphorus compounds, the intermediacy of pentacoordinate compounds has frequently been invoked[19-23]. The role of **8** and its analogues as fundamental reaction intermediates will be reported separately.



Scheme C

It should be noted that, in the reaction of 3-phenylpropynoic acid (**1**; $R = C_6H_5—C\equiv C—$) the anhydride **4** is not isolated but is converted under the reaction conditions to 1-phenylnaphthalene-2,3-dicarboxylic acid anhydride (**5**) in practically quantitative yield (Scheme D).



Scheme D

The present method for the preparation of anhydrides has the following advantages: (a) direct conversion of the acid **1** to the anhydride **4**, (b) mild reaction conditions, no heating and short reaction times, (c) the presence of electron-withdrawing or electron-donating groups does not effect the efficiency of the reaction, (d) sterically hindered carboxylic acids react to give the corresponding anhydrides in high yields, (e) the yields are high and reproducible, (f) the reagent **2** is readily prepared, and (g) no toxic, hazardous, or unstable materials are used as reagents and the experimental procedure is simple.

Melting points were determined with a Köfler microscope and are not corrected. I.R. spectra were obtained using a Beckmann Acculab 4 instrument and ^{1}H-N.M.R. spectra (60 MHz) using a Perkin-Elmer 462

Table 1. Anhydrides **4** from Carboxylic Acids **1** using Reagent **2**

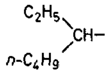
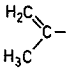
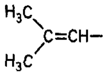
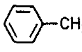
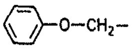
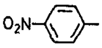
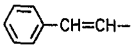
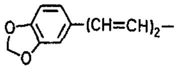
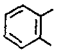
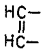
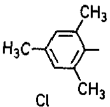
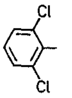
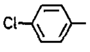
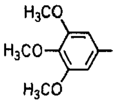
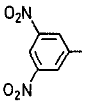
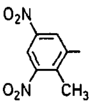
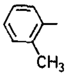
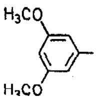
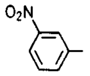
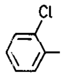
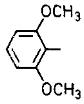
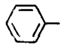
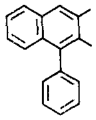
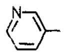
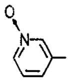
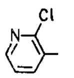
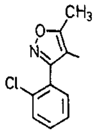
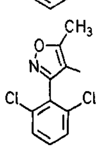
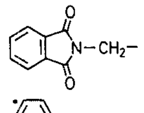
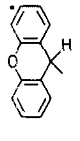
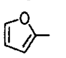
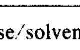
Entry	R	Base/ solvent system[a]	Reaction time [min]	Isolation method	Yield [%][b]	m.p. [°C] (solvent) or b.p. [°C]/torr	Molecular formula[c] or Lit. m.p. or b.p.	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]
1	$n\text{-}C_3H_7-$	I	30	B	95	199-201°/760	199.4-201.4°/760[24]	1821 (s), 1749 (m) (CH_2Cl_2)
2	$n\text{-}C_6H_{13}-$	I	30	B	97	170-173°/15	170-173°/15[24]	1824 (s), 1755 (m) (CH_2Cl_2)
3	 $(C_2H_5)(n\text{-}C_4H_9)CH-$	I	30	B	96	149-152°/8	149-152°/8[24]	1820 (m), 1759 (m)
4	$n\text{-}C_8H_{17}-$	I	45	B	96	18°	207°/15[24]	1825 (m), 1757 (m)
5	$n\text{-}C_{11}H_{23}-$	I	30	B	98	40-41°	42°[24]	1810 (m), 1745 (m)
6	$n\text{-}C_{15}H_{31}-$	I	45	B	94	63-64°	63.9°[24]	1810 (m), 1749 (m) (CCl_4)
7	$n\text{-}C_{17}H_{35}-$	I	30	B	97	69-71°	70.7°[24]	1826 (m), 1767 (m) (CCl_4)
8	$Br-CH_2-$	I	45	E	92	40-41°	40-42°[24]	1851 (m), 1768 (m)
9	$t\text{-}C_4H_9-$	I	180	E	90	78°/12	78°/12[24]	1815 (s), 1750 (m) (CCl_4)
10	 $H_2C=C(H_3C)-$	I	30	E	99	89°/5	89°/5[24]	1785 (s), 1725 (m)
11	$H_3C-CH=CH-$	I	30	E	100 (65)[26]	113-115°/12	113.5-114.5°/12[26]	1793 (s), 1738 (s)
12	 $(H_3C)_2C=CH-$	I	30	E	98 (65)[26]	77-80°/0.5	77-79°/0.5[26]	1785 (s), 1728 (s)
13		I	30	B	99	70-72° (ether)	72-72.5°[5]	1820 (s), 1741 (m)
14		I	30	B	95	67-68° (ether)	67-69°[24]	1820 (s), 1741 (m)
15		I	30	D	97	188-189°	189°[24]	1800 (s), 1740 (m) ($CHCl_3$)
16		I	30	B	97 (30)[14]	135-136° (acetone)	135-136°[24]	1770 (s), 1706 (s)
17		II	40	C	96	166-168° (CH_3CN)	$C_{24}H_{18}O_7$ (418.4)	1744 (m), 1717 (s)
18		I	60	B	98	127-130°	131°[24]	1855 (m), 1770 (s)
19	$HOOC-(CH_2)_4-$	I	60	B	99	71° (polymeric)	73-75° (polymeric)[27]	1815 (s), 1746 (m)
20	 $HC(-)=HC(-)$	I	60	B	82	115-117°	119°[24]	1877 (m), 1790 (s)
21		II	30	C	94	103-104° (CH_3CN)	$C_{20}H_{22}O_3$ (310.4)	1796 (s), 1738 (m)
22		III	240	C	91	155.5-156° (CH_3CN)	$C_{14}H_6Cl_4O_3$ (364.0)[d]	1822 (s), 1762 (m)
23		IV	30	C	97	193-194.5° (CH_3CN)	192-193°[10]	1783 (s), 1717 (s)
24		V	30	C	95	159.5-160° (CH_2Cl_2/CH_3CN)	158-160°[25,e]	1802 (s), 1726 (m)
25		VI	30	D	90 (55)[16]	220-223° (CH_3CN)	219-221°[24]	1811 (s), 1749 (m)
26		II	30	C	94	224-226° (CH_3NO_2)	$C_{16}H_{10}N_4O_{11}$ (434.3)	1800 (m), 1740 (m)
27		I	30	B	99	30-37° (*n*-hexane)	38-39°[24]	1798 (s), 1737 (m) (CH_2Cl_2)
28		VII	30	C	97	132-134° (CH_3CN)	134-135°[24]	1790 (s), 1722 (w)

Table 1. (Continued)

Entry	R	Base/ solvent system[a]	Reaction time [min]	Isolation method	Yield[b] [%]	m.p. [°C] (solvent) or b.p. [°C]/torr	Molecular formula[c] or Lit. m.p. or b.p.	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]
29		II	30	C	98	160–161.5° (CH_3CN)	160°[24]	1808 (s), 1742 (m)
30		VIII	30	C	94 (50)[11]	78.5–80° (*n*-hexane)	77–79°[11,f]	1777 (s), 1715 (m)
31		VI	45	B	97	159–160° (acetone/H_2O)	160°[12]	1799 (s), 1698 (m)
32		I	30	B	99	40–42°	40–42°[24]	1793 (s), 1730 (m) (CH_2Cl_2)
33[g]		I	45	D	97(90–95)[16]	260–262° (CH_3CN)	254–256°[16]	1830 (m), 1770 (s)
34		IX	30	A	96	122–123° (C_6H_6)	122.5–123.5°[5]	1801 (s), 1723 (s)
35		VI	150	D	88	199–210°	$C_{12}H_8N_2O_5$ (260.2)[h]	1814 (m), 1732 (m)
36		VIII	40	A	99	136–142° (CH_3CN)	$C_{12}H_6Cl_2N_2O_3$ (297.1)	1807 (s), 1740 (m)
37		VI	30	B	98	119–120°	122–124°[13]	1799 (s), 1736 (m)
38		VI	30	B	97	194–196° (CH_2Cl_2/*n*-heptane)	$C_{22}H_{14}Cl_4N_2O_5$ (528.2)	1786 (s), 1729 (m)
39		VI	30	D	97 (76)[14]	239–240°(O_2N—C_6H_5)	240–241°[29]	1848 (m), 1765 (m)
40		I	60	B	99	167–170° (CH_3CN)	$C_{28}H_{18}O_5$ (434.4)	1799 (s), 1744 (m)
41		I	30	D	75 (33)[16]	108–110°	$C_6H_6N_8O_3$ (238.2)	1832 (s), 1759 (m)
42		I	30	E	96 (64)[11]	71–72° (ether)	71–73°[11]	1782 (s), 1728 (m)

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[a] Base/solvent systems: I, $N(C_2H_5)_3/CH_2Cl_2$; II, $N(C_2H_5)_3/CH_3CN$; III, *N*-ethylpiperidine/CH_3CN; IV, $N(n\text{-}C_4H_9)_3/CH_3CN$; V, *N*-ethylpiperidine/acetone; VI, *N*-ethylpiperidine/CH_2Cl_2; VII, *N*-ethylpiperidine/dioxan; VIII, *N*-ethylpiperidine/THF; IX, $N(C_2H_5)_3$/THF.

[b] Literature yields given in brackets.

[c] Satisfactory microanalyses obtained (C ±0.4, H ±0.2, N ±0.3).

[d] ^{1}H-N.M.R. ($CDCl_3$): $\delta = 7.41$ ppm (s, 6 H_{arom}).

[e] ^{1}H-N.M.R. ($CDCl_3$): $\delta = 3.98$ ppm (s, 18 H, OCH_3).

[f] ^{1}H-N.M.R. ($CDCl_3$); $\delta = 7.52$, 8.52 ppm (2 m, 6 H_{arom}).

[g] Product from the reaction of **1** ($R = C_6H_5$—C≡C—), see Scheme **D**.

[h] ^{1}H-N.M.R. (DMSO-d_6): $\delta = 7.77$ (q), 8.55 (d, 8 H_{arom}).

instrument with TMS as internal standard. Technical grade carboxylic acids were used, solvents were dried by distillation from molecular sieves (Merck, perlform 4 and 3 Å). All experiments were performed with efficient magnetic stirring since the reaction takes place in the heterogeneous phase with respect to the reagent.

N,N-Bis[2-oxo-3-oxazolidinyl]phosphoramidic Chloride (2)[17]; Improved Procedure:

Phosphorus pentachloride (62.4 g, 0.30 mol) is added in one portion to a mixture of 2-oxo-1,3-oxazolidine (58.78 g, 0.675 mol) in acetonitrile (300 ml). The mixture is stirred at 20–25 °C for 24 h and is then cooled to −5 °C. Water (6 ml) is then added gradually and the temperature allowed to rise to 15-20 °C. After 30 min, the mixture is again cooled to −15 °C for 15 min. The white crystalline precipitate is filtered, washed with acetonitrile (25 ml), acetone (50 ml), and dried under vacuum; yield: 40.0 g (53%); m.p. 189-193 °C (dec); after recrystallization from acetonitrile, m.p. 195-198 °C; I.R. spectrum identical to that of an authentic sample.

The compound is pulverized for later use in the preparation of anhydrides and stored under anhydrous conditions.

Carboxylic Acid Anhydrides 4; General Procedure:

The salt of the carboxylic acid **1** is prepared by mixing the acid **1** (10 mmol) with the tertiary base (10 mmol) in an appropriate solvent (10 ml), see Table 1. To this solution is added reagent **2** (1.27 g, 5.0 mmol) and the suspension is stirred on a water bath at 20 °C for 5 to 15 min. One of the following work-up procedures is then applied:

A: Filtration of the salts and vacuum evaporation of the solvents;
B: Addition of aqueous sodium hydrogen carbonate solution (7 ml) at 0-5 °C, decantation of the aqueous phase, drying of the organic phase with magnesium sulfate or sodium sulfate, and evaporation of the solvent under reduced pressure;
C: Precipitation of the anhydride by addition of water (15 ml) at 0-5 °C;
D: Filtration of the reaction mixture; or
E: Vacuum evaporation of the reaction mixture and extraction of the anhydride with ether.

The dried product is then recrystallized and the soluble fraction recovered by evaporation of the solvent. The purity of the product was evaluated by the absence of the intense carbonyl band and of the signals of the coupled protons of the oxazolidine system. Microanalyses of the crude products indicated a maximum phosphorus content of 0.2-0.3%; in purified products the phosphorus content was found to be 4±4 ppm by X-ray fluorescence analysis and 2-4 ppm by colorimetric methods.

1(1*H*)-Tetrazolylacetic Anhydride:

To 1(1*H*)-tetrazolylacetic acid (1.39 g, 10.5 mmol) suspended in dichloromethane (10 ml), are successively added triethylamine (1.45 ml, 10.4 mmol) and reagent **2** (1.27 g, 5.0 mmol), the former at 10 °C and the latter after the solution has been warmed to 30 °C. The mixture is stirred for 30 min, the resultant white precipitate is filtered, washed with dichloromethane (5 ml), dried under vacuum at 40 °C to give the anhydride; yield: 0.89 g (75%); m.p. 108-110 °C (dec). *CAUTION! the product is explosive.*

1-Phenylnaphthalene-2,3-carboxylic Acid Anhydride (5):

To a dichloromethane solution (10 ml) of 3-phenylpropynoic acid (1.53 g, 10.5 mmol) and *N*-ethylpiperidine (1.46 ml, 10.5 mmol) at 20 °C is added reagent **2** (1.27 g, 5.0 mmol). The mixture is stirred for 45 min and then cooled to 5 °C. The white precipitate is filtered, washed with dichloromethane (8 ml), and dried under vacuum to give the product; yield: 1.06 g (77%). After extraction of the salts in the organic phase with water (10 ml), the organic phase is dried with sodium sulfate and evaporated under vacuum to give another crop of the product; yield: 0.27 g (20%); total yield: 1.33 g (97%); m.p. 260-262 °C (from acetonitrile); Ref.[16], m.p. 254-256 °C.

Similar results are obtained using triethylamine/acetonitrile; the reaction mixture is diluted with water and **5** isolated by filtration.

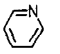
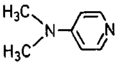
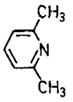
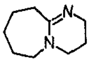
***N,N*-Bis[2-oxo-3-oxazolidinyl]phosphorodiamidic Acid (3):**

A mixture of the triethylamine or *N*-ethylpiperidine salt of the acid **3** and its hydrochloride is isolated by filtration, the former from the preparation of the anhydride in acetone and the salts from tetrahydrofuran solutions. The salt (~5 mmol) is dissolved in dichloromethane (15 ml) and a current of hydrogen chloride is bubbled through for 30 min. The precipitate is filtered, washed with dichloromethane, and dried to give the free acid; yield: 85-90%; white prisms; m.p. 153-154 °C (dec., from acetonitrile). The acid is soluble in water, insoluble in acetone, acetonitrile, and nitromethane.

$C_6H_9N_2O_6P \cdot 1.5H_2O$	calc.	C 27.4	H 4.6	N 10.6	P 11.8
(263.2)	found	27.2	4.3	10.6	11.8

I.R. (KBr): $\nu = 3450$, 1767 (d), 1718, 1397, 1263 cm^{-1}.

Table 2. Preparation of *p*-Chlorobenzoic Anhydride[a] (Effects of Solvent and Base)

Base	pK$_a$[28]	amount (mmol)	Solvent (ml)	Reaction time [min]	Yield [%]
$(C_2H_5)_3N$	10.8	10	CH_2Cl_2 (10)	5	80
		10	CH_3CN (10)	5	80
	5.3	31.3	CH_2Cl_2 (10)	1000	55
		31.3	CH_3CN (20)	180	70
	—	10	CH_2Cl_2 (10)	5	90
		10	CH_3CN (20)	5	90
	7.0	31.3	CH_2Cl_2 (10)	60	0
		31.3	CH_3CN (20)	60	61
	11.5	10	CH_3CN	5	90

[a] Reaction conditions: *p*-Cl—C_6H_4—COOH (10 mmol), reagent **2** (5 mmol), 20 °C, isolation of product by method C.

^{1}H-N.M.R. (D_2O): $\delta = 3.98$ (t, 4H, $J = 7$ Hz); 4.50 (t, 4H, $J = 7$ Hz); 4.82 ppm (s, 1 H).

Aroyl *N,N*-Bis[2-oxo-3-oxazolidinyl]phosphorodiamidates 8; Typical Procedure:

To a solution of 2,6-dichlorobenzoic acid (0.98 g, 5 mmol) in dichloromethane (15 ml) are added successively *N*-ethylpiperidine (0.70 ml, 5 mmol) and pulverized reagent **2** (1.27 g, 5 mmol). The mixture is stirred at 15 °C for 90 min. The mixture is then diluted with dichloromethane (10 ml), washed with water (15 ml), the organic phase is decanted, and dried with sodium sulfate. The solvent is removed by distillation under vacuum to give *2,6-dichlorobenzoyl* N,N*-bis[2-oxo-3-oxazolidinyl]phosphorodiamidate*; yield: 2.0 g (98%); m.p. 153.5-157 °C (dec); 154-154 °C (from dichloromethane/*n*-hexane).

$C_{13}H_{11}Cl_2N_2O_7P$	calc.	C 38.2	H 2.7	Cl 17.3	N 6.9	P 7.6
(409.1)	found	38.0	2.6	17.1	6.9	7.8

I.R. (KBr): $\nu = 1787$ (C=O), 1751 (COOP), 1217 cm^{-1} (P=O).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 4.30$ (t, 4H, $J = 7$ Hz); 4.55 (t, 4H, $J = 7$ Hz); 7.50 ppm (s, 3 H).

Reaction of this product with the triethylamine salt of the acid gave the anhydride.

As described above, 2,6-dinitrobenzoic acid (5 mmol) in acetonitrile (10 ml) is treated with triethylamine (5 mmol) and reagent **2**. The product, *2,6-dinitrobenzoyl* N,N*-bis[2-oxo-3-oxazolidinyl]phosphorodiamidate* is isolated by filtration; yield: 90%; m.p. 175-176 °C (dec, from acetonitrile); insoluble in dichloromethane.

$C_{13}H_{11}N_4O_{11}P$	calc.	C 36.3	H 2.6	N 13.0	P 7.2
(430.2)	found	35.9	2.5	12.5	7.4

I.R. (KBr): $\nu = 1780$ (C=O), 1758 (COOP), 1214 (P=O), 1545, 1355 cm^{-1} (NO_2).

^{1}H-N.M.R. (DMSO-d_6): $\delta = 3.95$ (t, 4H, $J = 7$ Hz); 4.21 (t, 4H, $J = 7$ Hz); 8.03, 8.6 ppm (m+t, 3 H).

Stirring of this product with aniline in dichloromethane for 100 min at 20 °C gives *2,6-dinitrobenzoylanilide*; yield: 100%; m.p. 218-220 °C (from ethanol).

$C_{13}H_9N_3O_5$	calc.	C 54.3	H 3.1	N 14.6
(287.2)	found	53.8	3.0	14.5

I.R. (KBr): $\nu = 3258$ (NH), 1655 (C=O), 1535, 1360 cm^{-1} (NO_2).

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