any statement concerning the decarboxylation of **5** is meaningless at this time, even though none of **11** was observed and one would have predicted a priori that **4** should decarboxylate more readily than **5** (for both electronic and steric reasons).

(7) The amount of **2a** and **10** generated by this treatment corresponded to only a very small amount (20–30%) of the molar quantity of **4** and **5** placed into the VPC instrument.

(8) P. S. Mayuranathan, *J. Chem. Soc.*, 493 (1957).

(9) R. Goncalves and E. V. Brown, *J. Org. Chem.*, **19**, 4 (1954).

(10) We could not determine by VPC if this material was the meta or para isomer or a mixture of both.

(11) These assignments are tentative as they were not confirmed by independent chemical analysis.

(12) R. L. Markezich, O. S. Zamek, P. E. Donahue, and F. J. Williams, *J. Org. Chem.*, this issue, companion paper. We also found that when 2 equiv of sodium nitrite are stirred with **1a** in DMF at room temperature, an immediate reaction began (in the form of violent bubbling and a color change from clear to dark yellow) and a 71% yield of the disodium salt of 3-nitrophthalic acid was obtained.

(13) This ratio was obtained by VPC analysis, ignoring possible detector response differences between the isomers. The ratio of products from ^{13}C analysis was 64:36.

(14) It has been reported in the literature that DMF will react with anhydrides at elevated temperatures to give dimethylamides: see G. M. Coppinger, *J. Am. Chem. Soc.*, **76**, 1372 (1954); H. Schindlbauer, *Monatsh. Chem.*, **99**, 1799 (1968); H. Schindlbauer, *ibid.*, **100**, 1583 (1969); H. Schindlbauer, *ibid.*, **104**, 848 (1973). Preliminary examination by ^{13}C NMR of our reaction mixtures indicated the presence of other new compounds in addition to the dimethylamide derivatives.

(15) This ratio was obtained by VPC analysis, ignoring possible detector response differences between the isomers. The ratio of products from ^{13}C analysis was 74:26.

(16) All vapor-phase chromatographic (VPC) analyses carried out in this section were conducted with a $\frac{1}{8}$ in. × 6 ft 10% SE-30 column programmed from 150 to 290 °C at 10°/min.

(17) These numbers did not take into account possible detector response differences for the isomers.

(18) K. Nakayawa and S. Baba, *J. Pharm. Soc. Jpn.*, **75**, 378 (1955).

(19) R. A. Heacock and D. H. Hey, *J. Chem. Soc.*, 2481 (1954).

(20) "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N.Y., 1965.

(21) G. H. Hurst and M. L. Bender, *J. Am. Chem. Soc.*, **93**, 704 (1971).

(22) For an example of these types of calculations using a substituent parameter approach, see ref 3. For further examples, see: G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, **94**, 3089 (1972); K. N. Scott, *ibid.*, **94**, 8564 (1972).

(23) This approach has been used successfully and tested using various pulse delays: see C. K. Sauers and H. M. Relles, *J. Am. Chem. Soc.*, **95**, 7731 (1973).

(24) G. C. Levy, private communication.

Reactions of Fluoride and Nitrite Ions with 4-Nitrophthalimides

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The reaction of 4-nitro-*N*-methylphthalimide with either fluoro or nitrite salts in an aprotic solvent affords up to a 78% yield of the diaryl ether, 4,4′-oxybis(*N*-methylphthalimide). When potassium fluoride is used in the reaction, 4-fluoro-*N*-methylphthalimide can also be isolated. The reaction of 4-fluoro-*N*-methylphthalimide with potassium nitrite affords the diaryl ether in 75% yield. A possible mechanism for the ether formation is discussed. The intermediate in this mechanism, 4-hydroxy-*N*-methylphthalimide, has been synthesized and shown to react with either 4-fluoro- or 4-nitro-*N*-methylphthalimide to afford the diaryl ether. In the reaction with 4-fluro-*N*-methylphthalimide, potassium fluoride was utilized as a base. Several other minor by-products were identified in the reaction; among them were *N*-methylphthalimide and 4-substituted phthalic acids. When Me_2SO is used as a solvent, 4-thiomethoxy-*N*-methylphthalimide is also formed.

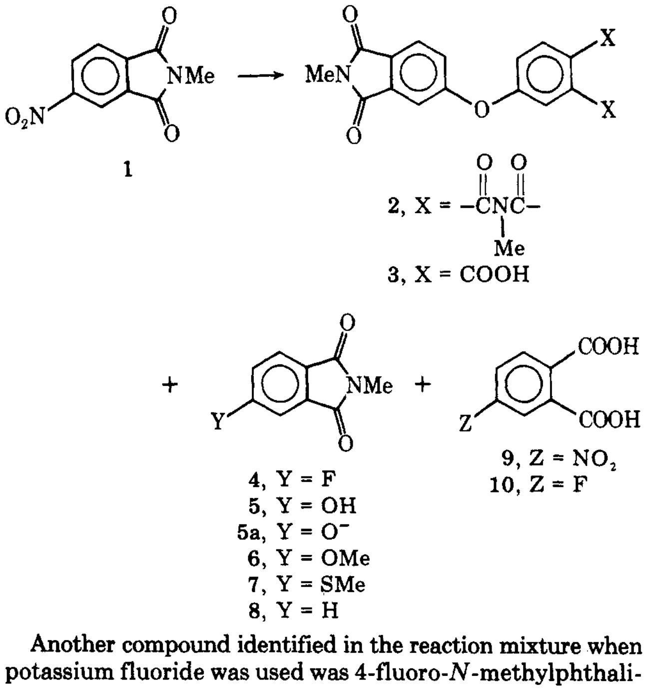
Recently[1] we reported the reaction of potassium fluoride with 4-nitrophthalic anhydride at elevated temperatures, in which a mixture of 4-fluorophthalic anhydride and dipotassium 4-nitrophthalate is produced. Reaction of 4-nitrophthalic anhydride with potassium nitrite produces dipotassium 4-nitrophthalate as the sole product. In this paper we describe the entirely different behavior of 4-nitro-*N*-methylphthalimide (**1**) with potassium fluoride and potassium nitrite.

Heating a solution of 4-nitro-*N*-methylphthalimide (**1**) with potassium fluoride in an aprotic solvent such as DMF, Me_2SO, or NMP at temperatures of 142–190 °C affords up to a 78% yield of 4,4′-oxybis(*N*-methylphthalimide) (**2**) (Scheme I). Instead of potassium fluoride, the use of potassium or sodium nitrite also affords good yields of the bisimide **2**. Examples are listed in Table I.

The reaction of nitro compounds to give diaryl ethers is not without precedent. It has been reported[2] that *p*-nitrobenzonitrile or *p*-chlorobenzonitrile will undergo a condensation reaction when treated with sodium nitrite in *N*-methylpyrrolidone to give 4,4′-oxybis(benzonitrile).

After isolation of the bisimide ether **2** by filtration, the filtrate was extracted with methylene chloride and the organic fractions were concentrated in vacuo. The components of this material were separated and identified by GC, GC/MS, and ^{13}C NMR analyses. The various products and their yields are listed in Table II.

Scheme I



2, X = $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\underset{\mathrm{Me}}{\underset{|}{\mathrm{N}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$

3, X = COOH

4, Y = F
5, Y = OH
5a, Y = O^-
6, Y = OMe
7, Y = SMe
8, Y = H

9, Z = NO_2
10, Z = F

Another compound identified in the reaction mixture when potassium fluoride was used was 4-fluoro-*N*-methylphthali-

Table I. Reaction of 4-Nitro-*N*-methylphthalimide (1) with Fluoride and Nitrite Salts

No.	Solvent	Salt	Equiv[a]	Time, h	Temp, °C	Yield of ether,[b] %
1	NMP	KF	1.6	8.5	190	72
2	NMP	KF	0.16	18	190	78
3	DMF	KF	1.0	16	153	69
4	Me_2SO	KF	0.9	18	142	42
5	Me_2SO	KF	1.0	19	142	61
6	Me_2SO	KF	2.0	28	142	52
7	Me_2SO	KF	4.0	28	142	47
8	DMF	NaF	1.0	16	153	<1
9	NMP	KNO_2	0.1	18	190	78
10	DMF	KNO_2	1.0	16	153	65
11	Me_2SO	KNO_2	1.0	18	142	50
12	DMF	$NaNO_2$	1.0	16	153	66

[a] Molar equivalents. [b] Isolated yield of 4,4′-oxybis(*N*-methylphthalimide) (2).

Table II. Yields[a] of Various Products Formed in the Reaction of 4-Nitro-*N*-methylphthalimide (1) with Fluoride and Nitrite Salts

		Compd yields, %										Total
No.[b]	Salt/solvent/time/temp	2[c]	1	4	5	7	8	9	3	6	10	yield, %
3	1.0 equiv KF/DMF/16 h/153 °C	70	7	7	1		1	6	1	Tr	1	94
4	0.9 equiv KF/Me_2SO/18 h/142 °C	39	7	22	3	3	1	4	1	Tr	Tr	80
7	4.0 equiv KF/Me_2SO/28 h/142 °C	45		8	1	13						67
10	1.0 equiv KNO_2/DMF/16 h/153 °C	65	5		2		3	14	4	Tr		93
11	1.0 equiv KNO_2/Me_2SO/18 h/142 °C	50	13		8	4	1	3	2	1		81
13[d]	1.1 equiv KNO_2/DMF/16 h/153 °C	75	4	4	4		4	6	1	Tr	Tr	98

[a] Absolute yields determined by ^{13}C NMR. [b] Experiment numbers are from Table I. [c] Yield of 2 was determined by isolation and VPC purity. [d] Reaction of 4-fluoro-*N*-methylphthalimide (4) with KNO_2.

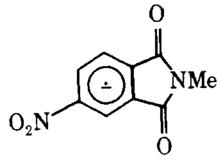
mide (4). This compound was not unexpected because treatment of 4-nitrophthalic anhydride with potassium fluoride afforded 4-fluorophthalic anhydride as the major product.[1] In one experiment, the methylene chloride extracts were distilled to afford an 8% yield of pure 4-fluoroimide (4). 4-Fluoro-*N*-methylphthalimide (4) was prepared in a 28% yield by heating neat 4-nitro-*N*-methylphthalimide (1) with potassium fluoride at 300 °C for 5 h and then distilling the product.

It is interesting at this point to compare the reactivity of 4-nitrophthalic anhydride with 4-nitro-*N*-methylphthalimide. Reaction of 4-nitrophthalic anhydride with potassium fluoride is complete within 25 min at 300 °C,[1] whereas 4-nitro-*N*-methylphthalimide requires more than 5 h under the same conditions and the yield of the 4-fluoro compound is much lower.

One of the more interesting compounds identified in the reaction mixture is 4-hydroxy-*N*-methylphthalimide (5). The phenol 5 is postulated as an intermediate in the formation of the bisimide 2 and will be discussed later. An authentic sample of 4-hydroxy-*N*-methylphthalimide (5) was prepared from 4-nitro-*N*-methylphthalimide by nitro displacement to afford a 74% yield of the methyl ether (6) followed by demethylation with boron tribromide to afford 5 in an 89% yield.

Another compound identified in the reaction mixture when Me_2SO was used as a reaction solvent was the thioether 7. An authentic sample of 7 was also prepared by nitro displacement. Treatment of 4-nitro-*N*-methylphthalimide (1) with the sodium salt of methyl mercaptan in DMF afforded a 76% yield of 4-thiomethoxy-*N*-methylphthalimide (7). It has been reported that the thermal decomposition of Me_2SO affords methyl mercaptan as one of the products.[3] Reaction of methyl mercaptan with either the 4-nitro compound 1 or the 4-fluoro compound 4 catalyzed by nitrite or fluoride salts would afford the methyl thioether 7.

4-Methoxy-*N*-methylphthalimide (6) was observed in most of the reactions, but it was formed in <1% yield and was not detectable by ^{13}C. Another compound produced in the reaction in small yield is *N*-methylphthalimide (8). It is probable that this compound is formed from the anion radical[4–6] 11 by loss of NO_2^- followed by hydrogen radical abstraction by the aryl radical.



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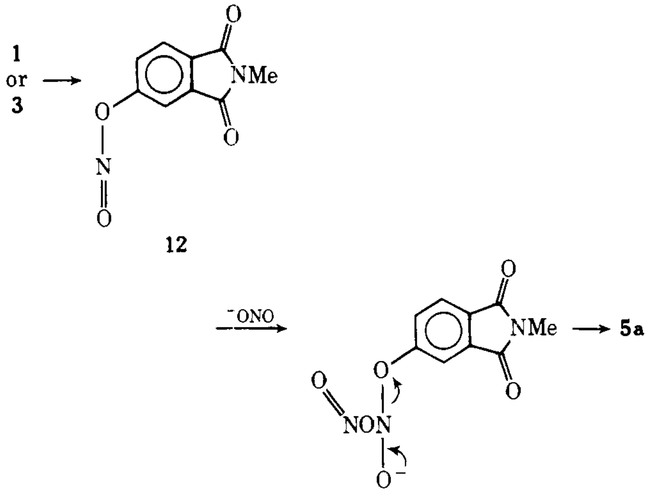
The diacids 3, 9, and 10 are also formed in the reaction of 4-nitro-*N*-methylphthalimide (1) with fluoride and nitrite salts. The formation of the diacids probably involve attack of nitrite ion on the carbonyl groups and then ring opening of the imide ring. We have shown that in the case of 4-nitrophthalic anhydride the only product of reaction with potassium nitrite is dipotassium 4-nitrophthalate.[1]

Reaction of 4-fluoro-*N*-methylphthalimide (4) with nitrite ion was also studied. Thus reaction of 4-fluoro-*N*-methylphthalimide (4) with potassium nitrite in DMF for 16 h at 153 °C gave a 74% yield of 4,4′-oxybis(*N*-methylphthalimide) (2). The other products identified in the reaction mixture are listed in Table II. Small amounts of 4-nitro-*N*-methylphthalimide (1) are observed, resulting from fluoro displacement by nitrite via nitrogen attack.

A possible mechanism for the formation of 4,4′-oxybis(*N*-methylphthalimide) (2) involves the intermediates 12 and 13 shown below. Nitrite ion has two potential reaction sites and can react by either oxygen or nitrogen attack.[7–9] Attack by oxygen on either 4-fluoro- or 4-nitro-*N*-methylphthalimide (4 or 1) gives the nitrite ester 12. Attack on 12 by another nitrite ion produces the phenoxide 5a and nitrogen oxides via the intermediate or transition state 13. Reaction of the phenoxide 5a with 4-fluoro- or 4-nitro-*N*-methylphthalimide (4 or 1) gives the ether 2.



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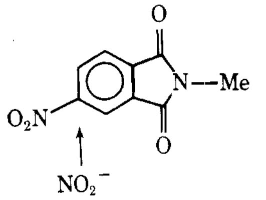
13

This mechanism is supported by Parker and co-workers,[10,11] who studied the reaction of nitrite ion with nitrohalobenzene to give nitrophenols. Two moles of nitrite ion were consumed per mole of nitrophenol produced. They detected no radicals (via ESR) and believed that the decomposition of the nitrite ester involved nucleophilic attack by NO_2^- on the nitrogen of ArONO to displace ArO^- and form N_2O_3.

We observed small amounts of 4-hydroxy-*N*-methylphthalimide (**5**) in the reaction mixtures. It has been well documented[12-17] that nitrobenzenes substituted by electron-withdrawing groups readily undergo displacement of the nitro group with a wide variety of nucleophiles. Activated fluorobenzenes will also undergo nucleophilic displacement of the fluoro group.[18] So, it is quite reasonable to assume that the phenoxide **5a** will displace the nitro or fluoro group from the substituted imide to afford the ether **2**. As a proof we ran displacement reactions with the phenol **5**. Reaction of 4-hydroxy-*N*-methylphthalimide (**5**) with 4-fluoro-*N*-methylphthalimide (**4**) in DMF containing potassium fluoride[19] gives an 82% yield of the ether **2**. Preforming the phenoxide of **5** with sodium hydride and then reaction with 4-nitro-*N*-methylphthalimide (**1**) gave an 81% yield of the ether **2**.

As has been reported,[1] 4-nitrophthalic anhydride, when treated with potassium nitrite, affords the dipotassium salt of 4-nitrophthalic acid; no 4,4′-oxybis(phthalic anhydride) was detected. The difference in reactivity of nitrite ion with 4-nitro-*N*-methylphthalimide and 4-nitrophthalic anhydride is striking. The two extreme cases of reactivity are shown (I and II). In the anhydride case, nitrite ion is trapped by reaction with the carbonyl groups to eventually give the diacid salt. In the *N*-methylimide case, the carbonyl groups being less reactive, nitrite ion is trapped by undergoing aromatic substitution to give a nitrite ester, which upon further reaction affords a phenoxide, which displaces a nitro group.



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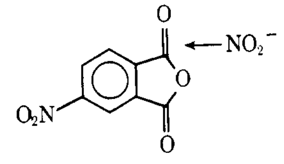

II

Experimental Section

General Procedures. All proton NMR spectra were measured on a Varian T-60 spectrometer with chemical shift values relative to tetramethylsilane. Carbon-13 NMR spectra were recorded on either a Varian XL-100-15 (25.2 MHz) or a Varian CFT-20 (20.0 MHz) NMR spectrometer operating in the Fourier transform (FT) mode with complete proton decoupling. Infrared spectra were measured on a Perkin-Elmer 457 grating infrared spectrophotometer. Mass spectra were obtained on a CEC 21-104 or a Varian MAT 311 spectrometer operating at 70 eV utilizing the direct inlet system. Vapor-phase chromatography (VPC) was carried out on a Hewlett-Packard 5700A gas chromatograph using a 6 ft × 1/8 in. 3% OV-17 on Chromosorb W column with temperature programming between 100 and 290 °C at 16°/min. Gas chromatography/mass spectroscopy was carried out on a Varian MAT 111 GC/mass spectrometer. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. All reactions were run under nitrogen unless otherwise noted. Anhydrous potassium fluoride was obtained from Alfa Chemicals.

Reaction of 4-Nitro-*N*-methylphthalimide (1) with Potassium Fluoride. In Me_2SO. A mixture of 22.421 g (109 mmol) of **1**, 14.757 g (254 mmol) of anhydrous KF, and 100 mL of dry Me_2SO was heated at 142 °C (bath temperature) with stirring for 27 h. The dark drown mixture, after cooling to room temperature, was poured into 900 mL of 0.2 M aqueous HCl to afford a brown precipitate. Filtration afforded 9.993 g (51% yield) of 4,4′-oxybis(*N*-methylphthalimide) (**2**) as a brown solid, mp 240–258 °C. Recrystallization from DMF afforded pale yellow prisms: mp 262–265 °C (lit.[24] mp > 250 °C]; ^{13}C NMR (Me_2SO-d_6) 23.2, 112.9, 123.7, 124.8, 128.1, 134.4, 160.1 ppm; ^1H NMR ($CDCl_3$) δ 3.18 (3 H, singlet), 7.3 (2 H, multiplet), 7.81 (1 H, apparent doublet, $J = 8.5$ Hz); IR (KBr) 1602, 1705, 1768, 1774 cm^{-1}; MS *m/e* 336 (100%, P^+), 308 (11%, P − CO), 292 (31%, P − CO_2).

Anal. Calcd for $C_{18}H_{12}N_2O_5$: 336.0746. Found: 336.0743.

The filtrate was extracted with dichloromethane and concentrated in vacuo to afford 6.383 g of a brown oil. Distillation gave 1.481 g (8% yield) of 4-fluoro-*N*-methylphthalimide (**4**) as a clear oil, bp 178–181 °C (30 mm), which solidified to a white solid on cooling, mp 99–100 °C.

The above reaction was repeated using 4.362 g (21.2 mmol) of **1**, 1.055 g (18.2 mmol) of anhydrous KF, and 40 mL of dry Me_2SO. This mixture was heated at 142 °C (bath temperature) with stirring for 18 h to afford 1.489 g (42% yield) of **2** as a light brown solid, mp 243–251 °C, 85% pure by VPC. The impurities were **1**, **4**, and **7**.

The filtrate was extracted twice with dichloromethane and concentrated in vacuo to afford 1.621 g of a brown oil. The ^{13}C NMR showed this oil to contain 54% **4**, 17% **1**, 10% **9**, 8% **5**, 5% **7**, 3% **8**, 2% **3**, and 1% **2**. The identity of these compounds was confirmed by GC/MS, which also showed the presence of **6** and **10**.

In DMF. The above reaction was repeated using DMF as a solvent. Heating a mixture of 5.177 g (25 mmol) of **1**, 1.536 g (26 mmole) of anhydrous KF, and 25 mL of dry DMF at reflux (153 °C) for 16 h afforded 2.900 g (69% yield) of **2** as a tan solid, mp 254–259 °C, >99% pure by VPC.

The filtrate was extracted with ethyl acetate and concentrated in vacuo to afford 1.247 g of a brown solid. The ^{13}C NMR spectrum showed it to consist of 30% **4**, 28% **1**, 24% **9**, 6% **8**, 4% **2**, 3% **5**, 3% **3**, and 2% **10**. The identity of these compounds was confirmed by GC/MS, which also showed the presence of **6**.

In NMP. A mixture of 10.227 g (50 mmol) of **1**, 4.559 g (79 mmol) of anhydrous KF, and 50 mL of dry NMP was heated at 190 °C (bath temperature) with stirring for 8.75 h. The dark brown mixture, after cooling to room temperature, was poured into 0.2 M aqueous HCl to afford 4.992 g (72% yield) of **2** as a tan solid, mp 259–263 °C.

Reaction of 4-Nitro-*N*-methylphthalimide (1) with Potassium Nitrite. In DMF. A mixture of 5.283 g (25.6 mmol) of **1**, 2.231 g (26.2 mmol) of potassium nitrite, and 25 mL of dry DMF was heated at reflux (153 °C) with stirring for 16 h. After cooling to room temperature the reaction mixture was poured into 100 mL of 0.2 M aqueous HCl to afford a tan precipitate. Filtration afforded 2.819 g (65% yield) of 4,4′-oxybis(*N*-methylphthalimide) (**2**) as a tan solid, mp 247–255 °C, >98% pure by VPC.

The filtrate was extracted twice with dichloromethane and concentrated in vacuo to afford 1.421 g of a brown oil. The ^{13}C NMR showed the oil to consist of 51% **9**, 20% **1**, 13% **8**, 9% **3**, and 8% **5**. The identity of these compounds was confirmed by GC/MS, which also showed the presence of **6** and **2**.

In Me_2SO. The above reaction was repeated using Me_2SO as a solvent. Heating a mixture of 4.013 g (19.5 mmol) of **1**, 1.644 g (19.3 mmol) of potassium nitrite, and 40 mL of dry Me_2SO at 142 °C (bath temperature) for 18 h afforded 1.638 g (50% yield) of **2** as a tan solid, mp 220–236 °C, 88% pure by VPC. The impurities were **1** and **7**.

The filtrate was extracted twice with dichloromethane and concentrated in vacuo to afford 1.241 g of a brown oil. The ^{13}C NMR showed the oil to contain 36% **1**, 25% **5**, 11% **9**, 10% **7**, 7% **2**, 4% **3**, 3% **8**, and 3% **6**. The identity of these compounds was confirmed by GC/MS.

Reaction of 4-Fluoro-*N*-methylphthalimide (4) with Potassium nitrite. A mixture of 1.674 g (9.4 mmol) of **4**, 0.840 g (9.9 mmol) of potassium nitrite, and 20 mL of dry DMF was heated at reflux (153

°C) with stirring for 16 h. After cooling to room temperature the reaction mixture was poured into 100 mL of 0.2 N aqueous HCl to afford a tan precipitate. Filtration afforded 1.164 g (74% yield) of 4,4′-oxybis(*N*-methylphthalimide) (**2**) as a light tan solid, mp 258–262 °C, >99% pure by VPC.

The filtrate was extracted with dichloromethane and concentrated in vacuo to afford 0.375 g of a brown gum. The ^{13}C NMR spectrum showed the mixture to consist of 25% **9**, 19% **5**, 19% **1**, 16% **4**, 16% **8**, 3% **2**, and 3% **3**. The identity of these compounds was confirmed by GC/MS, which also showed the presence of **10**.

4-Fluoro-*N*-methylphthalimide (4). A mixture of 21.30 g (103 mmol) of **1** and 12.02 g (207 mmol) of anhydrous KF was heated at 300 °C (bath temperature) for 5 h. After cooling to ~250 °C a still head was attached and the mixture distilled to afford 5.20 g (28% yield) of **4** as a clear liquid, bp 183–188 °C (60 mm), which on cooling solidified to an off-white solid: mp 98–100 °C; ^{13}C NMR (CDCl$_3$) 24.0, 110.4, 111.4, 120.4, 121.3, 125.4, 125.7, 128.2, 128.3, 135.0, 135.4, 161.3, 167.2, 171.5 ppm; ^{1}H NMR (CDCl$_3$) δ 3.20 (3 H, singlet), 7.2–8.0 (3 H, multiplet); IR (CHCl$_3$) 1612, 1713, 1769 cm^{-1}; MS *m/e* 179 (100%, P$^+$), 178 (16%), 151 (18%, P − CO), 135 (18%, P − CO$_2$), 122 (52%, P − CO − NMe).

Anal. Calcd for $C_9H_6NO_2F$: 179.0383. Found: 179.0386.

The pot residue (17.90 g) was placed in a Soxhlet extractor and extracted for 2 days with chloroform to afford 4.611 g of a brown solid. GC/MS analysis showed that this solid consisted of a mixture of **4**, **1**, and **2**.

4-Methoxy-*N*-methylphthalimide (6). To a mixture of 20.00 g (97 mmol) of **1** in 100 mL of dry Me$_2$SO was added 5.34 g (99 mmol) of sodium methoxide and the reaction stirred at room temperature for 1 h and then at 60–70 °C for 3 h. After cooling to room temperature, the mixture was poured into water and the precipitate filtered to afford 13.63 g (74% yield) of **6** as a tan solid. Recrystallization of a sample from ethyl acetate/hexane afforded tan needles; mp 153–155 °C (lit.[25] mp 153 °C); ^{13}C NMR (CDCl$_3$) 23.4, 55.5, 107.5, 118.9, 123.6, 123.6, 134.3, 164.0, 167.6 ppm; ^{1}H NMR (CDCl$_3$) δ 3.14 (3 H, singlet), 3.90 (3 H, singlet), 7.07 (1 H, doublet, $J = 8$ Hz), 7.22 (1 H, doublet, $J = 2$ Hz), 7.64 (1 H, quartet, $J = 2$ and 8 Hz); IR (CHCl$_3$) 1710, 1767 cm^{-1}; MS *m/e* 191 (100%, P$^+$), 190 (10%), 163 (18%, P − CO), 147 (36%, P − CO$_2$), 134 (30%, P − CO − NCH$_3$).

Anal. Calcd for $C_{10}H_9NO_3$: 191.0582. Found: 191.0585.

4-Hydroxy-*N*-methylphthalimide (5). To a mixture of 10.409 g (41.6 mmol) of boron tribromide in 50 mL of dichloromethane was added dropwise 1.596 g (8.4 mmol) of **6** in 50 mL of dichloromethane and the reaction mixture stirred overnight at room temperature. Water (~ 5 mL) was then added to hydrolyze the boron complexes and the dichloromethane was removed on a rotary evaporator. Filtration afforded 1.309 g (89% yield) of **5** as a light brown solid, mp 225–234 °C. Recrystallization of a sample from ethanol gave tan prisms: mp 244–246 °C [lit.[25] mp 250 °C); ^{13}C NMR (Me$_2$SO-d_6) 23.5, 109.7, 120.0, 122.0, 124.8, 134.5, 163.2, 167.8 ppm; ^{1}H NMR (Me$_2$SO-d_6) δ 3.00 (3 H, singlet), 7.1 (2 H, multiplet), 7.70 (1 H, apparent doublet, $J = 8.5$ Hz); IR (KBr) 1600, 1620, 1682, 1761 cm^{-1}; MS *m/e* 177 (100% P$^+$), 176 (13%), 149 (20%, P − CO), 133 (27%, P − CO$_2$).

Anal. Calcd for $C_9H_7NO_3$: 177.0426. Found: 177.0426.

4-Thiomethoxy-*N*-methylphthalimide (7). Into a 250-mL round-bottom flask fitted with a magnetic stirrer and nitrogen inlet was placed 4.332 g (102 mmol) of 56.8% NaH oil dispersion. After washing with hexane, 100 mL of dry DMF was added, and then methyl mercaptan was bubbled into the mixture until hydrogen evolution ceased. To this was added 20.00 g (97 mmol) of **1** and the reaction was stirred at room temperature overnight. The reaction mixture was then poured into water and filtered to afford 15.542 g (76%) of **7** as a light tan solid, mp 141–143 °C. Recrystallization of a sample from ethyl acetate/hexane afforded pastel yellow prisms: mp 142–144 °C; ^{13}C NMR (CDCl$_3$) 14.9, 23.6, 119.1, 122.8, 127.8, 129.8, 132.9, 147.6, 167.7 ppm; ^{1}H NMR (CDCl$_3$) δ 2.55 (3 H, singlet), 3.13 (3 H, singlet), 7.5 (3 H, multiplet); IR (CHCl$_3$) 1604, 1702, 1769 cm^{-1}; MS *m/e* 207 (100%, P$^+$), 163 (32%, P − CO$_2$).

Anal. Calcd for $C_{10}H_9NO_2S$: 207.0354. Found: 207.0349.

Reaction of 4-Hydroxy-*N*-methylphthalimide (5) with 4-Fluoro-*N*-methylphthalimide (4). A mixture of 0.931 g (5.3 mmol) of **5**, 0.965 g (5.4 mmol) of **4**, 0.332 g (5.7 mmol) of anhydrous KF, and 20 mL of dry DMF was stirred and heated at reflux (153 °C) for 16 h. After cooling to room temperature the reaction mixture was poured into 100 mL of 0.2 M aqueous HCl to give a tan precipitate. Filtration afforded 1.461 g (82% yield) of 4,4′-oxybis(*N*-methylphthalimide) (**2**) as a tan solid, mp 265–267.5 °C, >99% pure by VPC.

Reaction of 4-Hydroxy-*N*-methylphthalimide (5) with 4-Nitro-*N*-methylphthalimide (1). Into a round-bottom flask was placed 1.064 g (6.04 mmol) of **5**, 0.689 g (6.14 mmol) of potassium *tert*-butoxide, and 20 mL of dry DMF. After stirring at room temperature for 30 min to form the phenoxide, 1.288 g (6.25 mmol) of **1** was added. The reaction mixture was stirred and heated at reflux (153 °C) for 16 h. After cooling to room temperature the reaction mixture was poured into 100 mL of 0.2 M aqueous HCl to give a tan precipitate. Filtration afforded 1.651 g (81% yield) of 4,4′-oxybis(*N*-methylphthalimide) (**2**) as a tan solid, mp 266–268 °C, >99% pure by VPC.

Registry No.—**1**, 41663-84-7; **2**, 27507-54-6; **3**, 63196-43-0, **4**, 63196-44-1; **5**, 4112-65-6; **6**, 63196-45-2; **7**, 63196-46-3; **8**, 550-44-7; **9**, 610-27-5; **10**, 320-97-8; KF, 7789-23-3; NaF, 7681-49-4; KNO$_2$, 7758-09-0; NaNO$_2$, 7632-00-0; sodium methoxide, 124-41-4; methyl mercaptan, 74-93-1.

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