The product was sublimed and then Soxhlet extracted with hexane to give 13.34 g (80%) of pure dichloromaleic anhydride, mp 118–120° (lit.[19] 119°). It was further identified unequivocally by mass spectrometry: molecular-ion two-chlorine cluster at m/e 166–170 and appropriate peaks and chlorine clusters for $M - CO_2$, $M - CO_2 - CO$, $M - CO_2 - Cl$, C_2Cl, C_3O, CCl, and C_2.

Control Experiments. A.—No reaction could be detected (nmr) between **2a** (1.73 g) (vinyl, s, δ 6.83, 2 H; aromatic, m, centered at δ 7.40, 5 H) and thionyl chloride (4 ml) in methylene chloride (20 ml) during 16 hr at 25°.

B.—No reaction could be detected by nmr spectroscopy between **2a** (1.73 g) (vinyl, s, δ 6.75, 2 H; aromatic, m, centered at δ 7.33, 5 H) and thionyl chloride (20 ml) (homogeneous solution) during 19 hr at 25° or 3 hr at reflux (~80°).

C.—No reaction could be detected (nmr) between pyridine (0.87 g) (β protons, m, δ 7.27–7.62, 2 H; γ protons, m, δ 7.62–8.06, 1 H; α protons, m, δ 8.55–8.80, 2 H) and thionyl chloride (20 ml) during 17.5 hr at 25°.[3]

D.—No reaction could be detected (nmr) between pyridine (0.79 g) (α protons, m, δ 8.17–8.44, 2 H) and **2a** (1.73 g) (vinyl, s, δ 6.90, 2 H) in anhydrous dimethyl sulfoxide (20 ml) during 17 hr at 25°.

E.—No reaction could be detected (nmr) between thionyl chloride and **2b**, **4a**, **4b**, **4c**, or **6** during several hours at 25–35°.

F.—The nmr spectrum of **2c** in thionyl chloride (vinyl, d, J = 1.2 Hz, 2 H, coupling with NH; NH, very broad peak, δ 7.90, 1 H) remained unchanged during several hours at 25–35°.

Registry No.—**3a**, 3876-05-9; **5a**, 35740-25-1; **5b**, 35740-26-2; **5c**, 19544-45-7; **8**, 35725-75-8; **8** BF_4, 35740-74-0; **11**, 35740-28-4; $SOCl_2$, 7719-09-7; pyridine, 110-86-1.

Acknowledgments.—The author wishes to thank J. V. Crivello for generous gifts of **4a**, **4b**, and **4c** and Professor D. M. Lemal for copies of infrared and nmr spectra of **16**.

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[19] T. Zincke and O. Fuchs, *Justus Liebigs Ann. Chem.*, 267, 20 (1891).

Dichloromaleimide Chemistry. III. The Reaction of *N*-Aryldichloromaleimide with Phenols. The Preparation and Mass Spectral Rearrangements of *N*-Aryl-3-aryloxy-4-chloromaleimides and *N*-Aryl-3,4-bis(aryloxy)maleimides

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N-Aryldichloromaleimides have been found to react with substituted phenols under basic conditions to give aryloxychloro and/or bisaryloxy substituted maleimides, depending on the base/solvent system employed. A hindered phenol (2,6-dimethylphenol) was observed to undergo some carbon alkylation in its reaction with *N*-phenyldichloromaleimide. The mechanisms of these reactions (and some side reactions) are discussed, as are the ^{13}C nmr and mass spectra of many of the products.

A few examples of the displacement of chloride by nucleophiles in *N*-substituted dichloromaleimides have appeared in the literature in recent years. In the reaction with primary amines,[1] displacement of one chlorine occurred together with transimidation. In all other cases, a chlorine was displaced by a group (–CN,[2] –SO_2R,[2] –SR,[3] and –NR_3^+[4]) which subsequently facilitated the displacement of the second chlorine, presumably through its ability to stabilize an α-carbanionic center.[5] The reactions of phenols with N-substituted dichloromaleimides have not been reported previously.[6] In this paper we discuss these reactions in detail as well as the mass spectra of the products produced therein.

Results and Discussion

When *N*-aryldichloromaleimides **1a–h** were treated with phenols in the presence of base, a facile reaction ensued which led first to *N*-aryl-3-aryloxy-4-chloromaleimides (**2**) and then to *N*-aryl-3,4-bis(aryloxy)maleimides (**3**). In certain base/solvent systems this condensation could be carried out to give only **2** with total exclusion of further reaction. For example, when a methylene chloride solution of *N*-phenyl-3,4-dichloromaleimide **1d** (1 mol), 4-methylphenol (4 mol), and triethylamine (3 mol) was stirred at *ca.* 25° for 2 hr, the only product formed in >99% yield was *N*-phenyl-3-(4-methylphenoxy)-4-chloromaleimide **2dj**; no detectable amount of *N*-phenyl-3,4-bis(4-methylphenoxy)maleimide **3dj** was formed. Similarly, a 1:1 mixture of **1d** and 4-methylphenol in methylene chloride in the presence of an excess of potassium carbonate gave only **2dj**.

Most of the *N*-aryl-3-aryloxy-4-chloromaleimides (**2**) (see the first column of Table II) were prepared under similar reaction conditions (see Experimental Section) and were not contaminated with any other products. A few (**2bk**, **2dp**, **2gj**, and **2hp**) were prepared using K_2CO_3 or Na_2CO_3 in *N,N*-dimethylformamide (DMF); side reactions (*vide infra*) were minimized by appropriately limiting the reaction times in these

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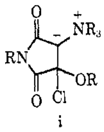
[1] R. Oda, Y. Hayashi, and T. Takai, *Tetrahedron*, **24**, 4051 (1968).

[2] E. L. Martin, C. L. Dickinson, and J. R. Roland, *J. Org. Chem.*, **26**, 2032 (1961).

[3] (a) K. Fickentscher, *Tetrahedron Lett.*, 4273 (1969); (b) P. Dimroth and F. Reicheneder, *Angew. Chem., Int. Ed. Engl.*, **8**, 751 (1969).

[4] M. J. Karten, S. L. Shapiro, E. S. Isaacs, and L. Freedman, *J. Org. Chem.*, **30**, 2657 (1965).

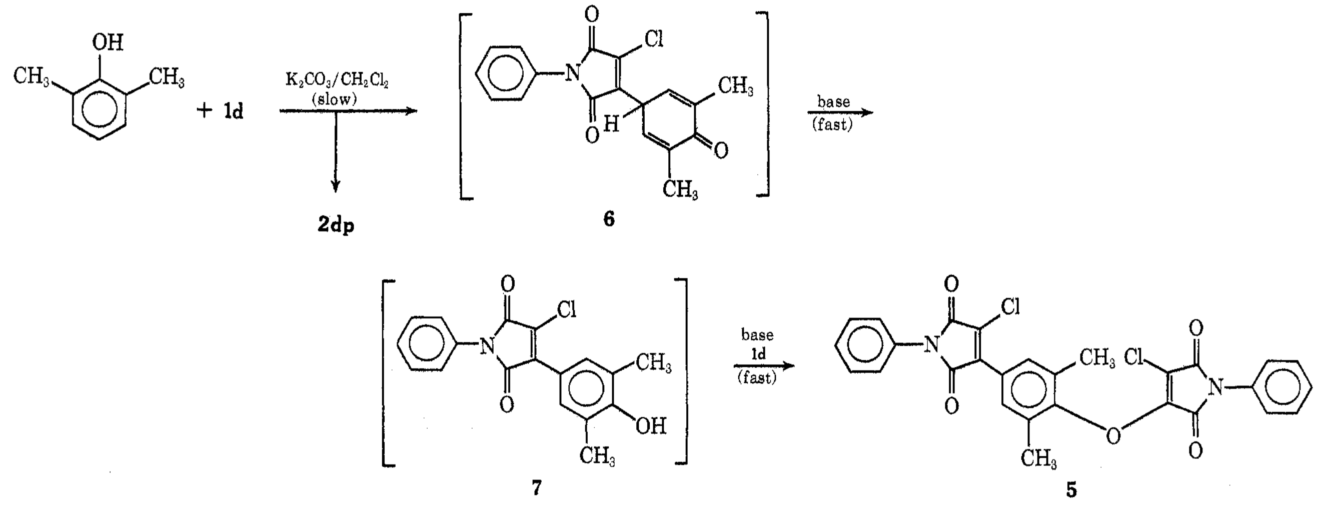
[5] For example, a probable structure for one intermediate in the reactions of Karten, *et al.*,[4] is i.

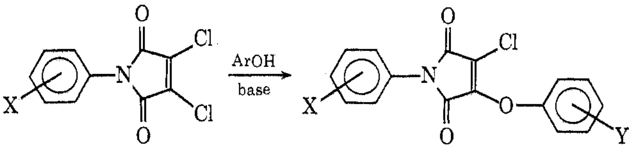


i

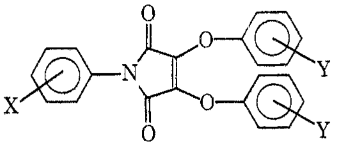
[6] Brief mention, with no experimental details, was made[2] of a reaction which takes place between phenols, *N*-phenyldichloromaleimide, and presumably sodium cyanide.

SCHEME I





2

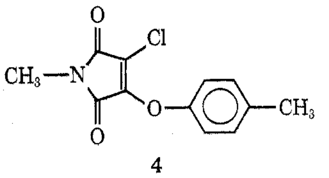


3

a, X = *p*-OCH$_3$
b, X = *p*-OC$_6$H$_5$
c, X = *p*-CH$_3$
d, X = H
e, X = *p*-Cl
f, X = *m*-Cl
g, X = *p*-CN
h, X = 2,6-di-CH$_3$

i, Y = *p*-OCH$_3$
j, Y = *p*-CH$_3$
k, Y = H
l, Y = *p*-Cl
m, Y = *m*-Br
n, Y = *p*-CN
p, Y = 2,6-di-CH$_3$

cases. *N*-Methyl-3-(4-methylphenoxy)-4-chloromaleimide **4** was obtained with K$_2$CO$_3$ in methylene chloride from *N*-methyl-3,4-dichloromaleimide and 4-methylphenol.

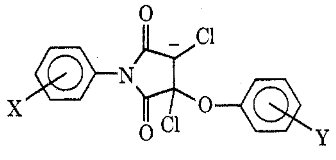


4

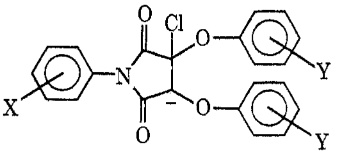
Although **2dp** was readily prepared with Na$_2$CO$_3$ in DMF, the use of K$_2$CO$_3$ in CH$_2$Cl$_2$ solution led to a mixture of **2dp** and **5**. Apparently, with the hindered 2,6-dimethylphenol, some competititive para-carbon alkylation occurred, presumably leading to **7** *via* **6** (Scheme I) and thereafter to **5** with a second molecule of **1d**. The failure to observe any of **7** is perhaps not surprising since its increased acidity would allow it to react much more rapidly with the base (and then with **1d**) than 2,6-dimethylphenol and thus prevent its buildup over the course of this particularly slow overall reaction (~11 days at 25°).

Under strongly basic conditions, both chlorines of **1** could be displaced quantitatively. Thus, **3aj**, **3dj**, and **3hj** were the only products obtained from the rapid reactions of **1a**, **1d**, and **1h**, respectively, with 2 equiv of sodium 4-methylphenoxide in DMSO or DMSO–chlorobenzene. **3dk** was similarly obtained from **1d** and 2 equiv of sodium phenoxide.

The facility with which aryl oxide displaced one chlorine from **1** relative to that for the chlorine of **2** is undoubtedly due to a combination of factors. Comparing the two presumed intermediates (**8** and **9**) in



8



9

these cases, it is clear that steric requirements for the formation of **9** would be much greater than that for **8**. Similarly, inductive effects for chlorine and phenoxy (Cl, σ^*[7] 1.05; C$_6$H$_5$O, 0.85) would be expected to result in an increase in the stability of the carbanionic center in **8** compared with that in **9**, but stronger evidence bearing on this matter was obtained from the infrared and ^{13}C nmr spectra of **2**. The infrared spectrum of all structures **2** displayed two strong carbonyl absorptions: one at 1720–1731 cm^{-1} for the carbonyl group adjacent to the aryloxy group and one at 1648–1654 cm^{-1} for the carbonyl group conjugated with the aryloxy-ether oxygen. Such conjugation, as depicted in the hybrid contributors **10** and **11**, would be expected to lead to increased electron density at the chlorine-bearing carbon, thereby decreasing the tendency for a nucleophile, such as an aryloxide ion, to attack at that position. Likewise, ^{13}C nmr spectra of **2aj**, **2dj**, **2dk**,

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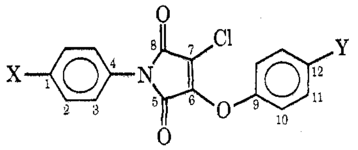
[7] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 595.

TABLE I

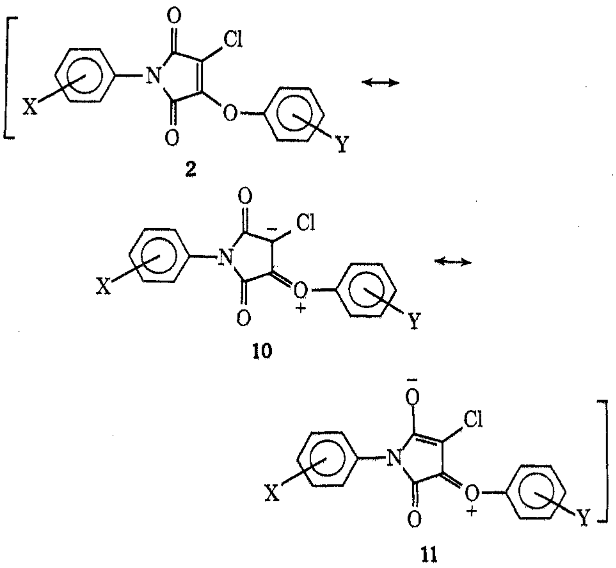
^{13}C NMR SPECTRA[a] AND PROBABLE ASSIGNMENTS[b]



Compd	X	Y	Carbon atom 1	2	3	4	5 and 8	6	7	9	10	11	12	In X	In Y
2aj	CH_3O-	CH_3	159.0	114.3	128.5	123.5	162.8, 164.3	148.3	109.5	151.5	118.7	130.1	135.0	55.4	20.3
2dj	H	CH_3	128.1	129.0	126.9	131.1	162.5, 164.1	148.4	109.6	151.5	118.8	130.1	135.0		20.3
2dk	H	H	128.2	129.0	126.9	131.0	162.5, 163.9	148.1	110.6	153.7	118.8	129.8	125.7		
2ej	-Cl	CH_3	129.9	(129.1 or 128.5)		132.7	162.3, 163.8	148.5	109.8	151.5	118.7	130.1	135.1		20.3
2gj	-CN	CH_3	10.4	133.2	126.8	*c*	162.0, 163.6	148.6	110.1	151.5	118.8	130.2	135.2	118.3	20.4

[a] Determined in DMSO-d_6. The chemical shifts given are in parts per million downfield from internal TMS. [b] Personal communication: G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, **94**, 3089 (1972). [c] Probably obscured by the peak for carbon atom 12 at 135.2 ppm; the chemical shifts of each carbon atom 4 in this table are very nearly the same as those for the same carbon atom in the corresponding *N*-aryldichloromaleimides: **1a**, 124.0; **1d**, 131.7; **1e**, 134.0; **1g**, 136.3 ppm in DMSO-d_6 (see ref 8).

2ej, and **2gj** (see Table I) further suggest the importance of the resonance hybrid contributor **10**. The chemical shift of the chlorine-bearing carbon in these structures (in DMSO-d_6) occurs at 109.5–110.6 ppm while those in the corresponding dichloromaleimide structures **1a**, **1d**, **1e**, and **1g** occur at 133.1–134.2 ppm.[8,9]



2

10

11

The reaction of **2fi** with 4-chlorophenoxide led to a mixture of **3fi**, **15**, and **3fl**. These results can be interpreted to indicate that the rate of attack on the chlorine-bearing carbon was slow compared to that on the aryloxy-bearing carbon to give an intermediate **13** (Scheme II) even though the formation of such an intermediate would be accompanied by strong steric interactions. Dissociation of **13** back to starting materials or to **2fl** and **14** would provide all the necessary reactants to give the final product mixture.

Although the reactions discussed thus far were relatively straightforward, resulting either in displacement of exactly one chlorine (weakly basic conditions such as K_2CO_3/CH_2Cl_2) or exactly two chlorines (strongly basic conditions such as NaOAr/DMSO), reaction conditions were also investigated which led to facile displacement of one chlorine followed by a much slower displacement of the second. (In fact, **2bk**, **2dp**, **2gj**, and **2hp** were prepared by such a method under controlled conditions; see Experimental Section.) Under these conditions, a side reaction, namely imide-ring hydrolysis, became competitive with the slow rate of displacement of the second chlorine. For example, in the reaction of calcium oxide with **1d** and 2 equiv of 4-methylphenol in DMF, rapid formation of **2dj** was followed by hydrolysis of **2dj**, formation of some **3dj**, and hydrolysis of **3dj**. The thermal behavior (during vapor phase chromatographic analysis) of these hydrolysis products was of interest since it allowed a complete analysis of the changing complex reaction mixture. At ~350° (injection port temperature), the amic acids lost aniline to give anhydrides **16**[10a] and **17**[10b] (isolated and identified by nmr and/or mass spectra) while the silylated amic acids lost presumably trimethylsilanol [or bis(trimethylsilyl) ether] to give **2dj** and **3dj**. Control experiments[11] showed that **1d**, **2dj**, and **3dj** were each stable in DMF solution in the presence of CaO, $Ca(OH)_2$, and $CaO/Ca(OH)_2/CaCl_2$. In the presence of the mixture of calcium salts *and* 4-methylphenol, **2dj** underwent hydrolysis to amic acid(s) (which gave **16** thermally, vpc) as well as slow conversion to **3dj** followed by hydrolysis of the latter to an amic acid (which gave **17** thermally, vpc). Similarly, the calcium salt mixture *and* 4-methylphenol caused **3dj** to undergo hydrolysis to an amic acid (which gave **17** thermally, vpc). Perhaps a *soluble* calcium hydroxide, such as $Ca(OH)(OC_6H_5CH_3)$, is implicated by these experiments. These results are summarized in Scheme III. Similar hydrolysis and thermal behavior was observed for other reactions with other inorganic bases in DMF (see Experimental Section).

Mass Spectra.—We have recently reported[8] our observations on the mass spectral rearrangement and cleavage of *N*-aryldichloromaleimides, **1**. We now wish to disclose the mass spectral behavior of the two new related classes of *N*-aryl-disubstituted maleimides, **2** and **3**; the salient features of the spectra are listed in Tables II and III, respectively.

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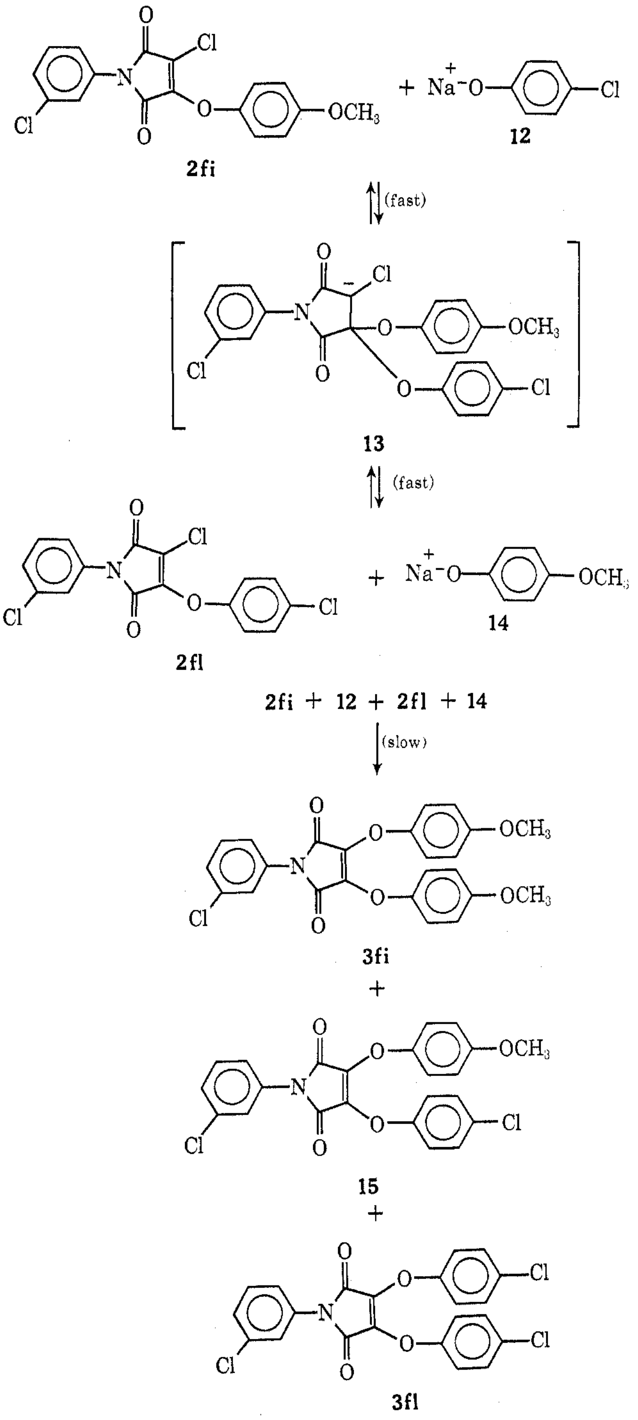
(8) H. M. Relles and R. W. Schluenz, *J. Org. Chem.*, **37**, 1742 (1972).

(9) Similar differences have been reported in the ^{13}C nmr spectra of vinyl ethers and their corresponding olefins: K. Hatada, K. Nagata, and H. Yuki, *Bull. Chem. Soc. Jap.*, **43**, 3195 (1970).

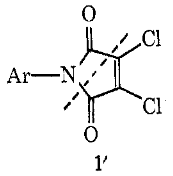
(10) (a) This anhydride was also isolated by preparative vpc (and identified by its mass spectrum) during a preparation of **2gj** with Na_2CO_3 in DMF.[11] In this case, 4-cyanoaniline was the other thermally produced product (vpc). (b) This anhydride was also isolated by preparative vpc (and identified by its mass spectrum) during a preparation of **2hj** and **3hj** with Na_2CO_3 in DMF.[11] Here, 2,6-dimethylaniline was also produced.

(11) H. M. Relles, unpublished results.

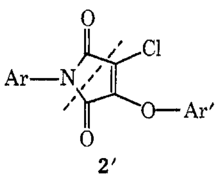
SCHEME II



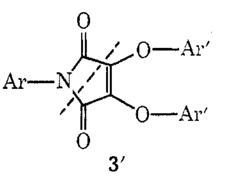
These spectra contrast in several ways with those reported[8] for **1**. All three structural types showed prominent cleavage giving rise to $(ArNCO)^+$ ions (see **1′**, **2′**, and **3′**), but only in the case of **1** did the other portion of the molecule (produced by this cleavage) also appear as a prominent ion, $(C_3Cl_2O)^+$; in none of the compounds **2** or **3** were there any peaks corresponding to $(C_3ClO_2Ar')^+$ or $(C_3O_3Ar'_2)$,$^+$ respectively.



1′



2′



3′

Other gross differences occurred because of the variety of rearrangement paths available to **2** and **3** (as a result of the presence of –OAr′ groups) which were not available in **1**. Of interest in the case of **2** were the rearrangement-cleavage ions $(M - C_3ClO_2)^+$ and $(M - C_4ClO_3)^+$. The fact that the portion lost from the former (C_3ClO_2) also occurred as a major ion in all of the spectra (and in many cases as the base peak) may be of significance for a mechanistic rationale of these rearrangement processes. One such possible rationale is illustrated in Scheme IV. The mechanism depicted also explains the prominent rearrangement-cleavage ions $(M - C_3O_3Ar')^+$, $(C_3O_3Ar')^+$, and $(M - C_4O_4Ar')^+$ of structure **3** if each chlorine is replaced in this scheme with an OAr′ group.

Experimental Section

All ^1H nmr spectra were recorded with a Varian Associates T-60 nmr spectrometer using tetramethylsilane as an external standard and deuteriochloroform as solvent, unless noted otherwise. All ^{13}C nmr spectra were recorded with a Varian Associates XL-100-15 nmr spectrometer using complete ^1H decoupling at 100 MHz with simultaneous ^{13}C observation at 25.2 MHz. Chemical shifts were measured from internal tetramethylsilane or calibrated to this standard using known chemical shifts of solvent peaks. Mass spectra were determined on a C. E. C. 21-104 analytical mass spectrometer at 70 eV. Infrared spectra were taken as KBr pellets unless noted otherwise. Vapor-phase chromatography (vpc) was carried out on a Hewlett-Packard 5750 with 6 ft 10% SE-30 silicone gum rubber columns and temperature programming from 200–290° at 10°/min; injection port temperature was 350°. All of the dichloromaleimides used herein were prepared from the appropriate amine and dichloromaleic anhydride in refluxing glacial acetic acid.[8] The synthesis of one not reported previously is given below. Anhydrous DMSO and DMF were obtained by distillation from CaH_2, at reduced pressure and atmospheric pressure, respectively.

Preparation of *N*-(2,6-Dimethylphenyl)dichloromaleimide, 1h.—A solution of 24.2 g (0.20 mol) of 2,6-dimethylaniline in 150 ml of acetic acid was added slowly (30 min) to 50.1 g (0.30 mol) of dichloromaleic anhydride in 300 ml of acetic acid. Much precipitate formed during this addition which was presumably the amide acid.[12] The system was refluxed for 1 hr and cooled, and the solid product which had crystallized was filtered. A second batch of solid product was obtained by adding 300 ml of water to the above filtrate. The total product was recrystallized from hexane giving 46.1 g (85%) of **1h**: mp 140.5–141.5°; mass spectrum *m/e* [rel intensity, assignment]; 269 [100, M^+], 190 [50, $(M - CO_2 - Cl)^+$],[8] 147 [9.0, $(M - C_3Cl_2O)^+$],[8] 146 [16.5, $M - C_3Cl_2O - H)^+$], 122 (3.5, $(C_3Cl_2O)^+$].[8]

Anal. Calcd for $C_{12}H_9Cl_2NO_2$: Cl, 26.3. Found: Cl, 26.2.

***N*-(4-Methoxyphenyl)-3-(4-methylphenoxy)-4-chloromaleimide, 2aj.**—A solution of 27.21 g (0.10 mol) of *N*-(4-methoxyphenyl)-3,4-dichloromaleimide, **1a**, and 10.81 g (0.10 mol) of 4-methylphenol in 250 ml of methylene chloride was stirred for 3 days at ~25° with 69.1 g (0.50 mol) of anhydrous K_2CO_3. The system was added with caution (CO_2 evolution) to excess 1 *N* HCl and an additional 250 ml of CH_2Cl_2. The resulting organic phase was extracted with water, dried ($MgSO_4$), and freed of solvent *in vacuo*. Recrystallization of the product (cyclohexane) gave 28.9 g (84%) of **2aj**: mp 155.0–155.5°; ^1H nmr spectrum δ 6.67–7.28 (m, 8, aromatic), 3.70 (s, 3, CH_3O), and 2.30 (s, 3, CH_3Ar); ir 1648 and 1720 cm^{-1} (two C=O). The ^{13}C nmr spectrum and mass spectrum were also in accord with the product and are given in Tables I and II, respectively.

Anal. Calcd for $C_{18}H_{14}ClNO_4$: C, 63.0; H, 4.11; N, 4.08. Found: C, 63.7; H, 4.0; N, 4.0.

***N*-(4-Methoxyphenyl)-3,4-bis(4-methylphenoxy)maleimide, 3aj.**—Exactly 1.60 g of 50.0% aqueous sodium hydroxide (0.020 mol of NaOH) was added to 2.16 g (0.020 mol) of 4-methylphenol

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[12] In many similar preparations of other *N*-aryldichloromaleimides, this initially formed solid dissolved when the system was heated and another solid crystallized from solution at reflux which eventually proved to be the imide product.

SCHEME III

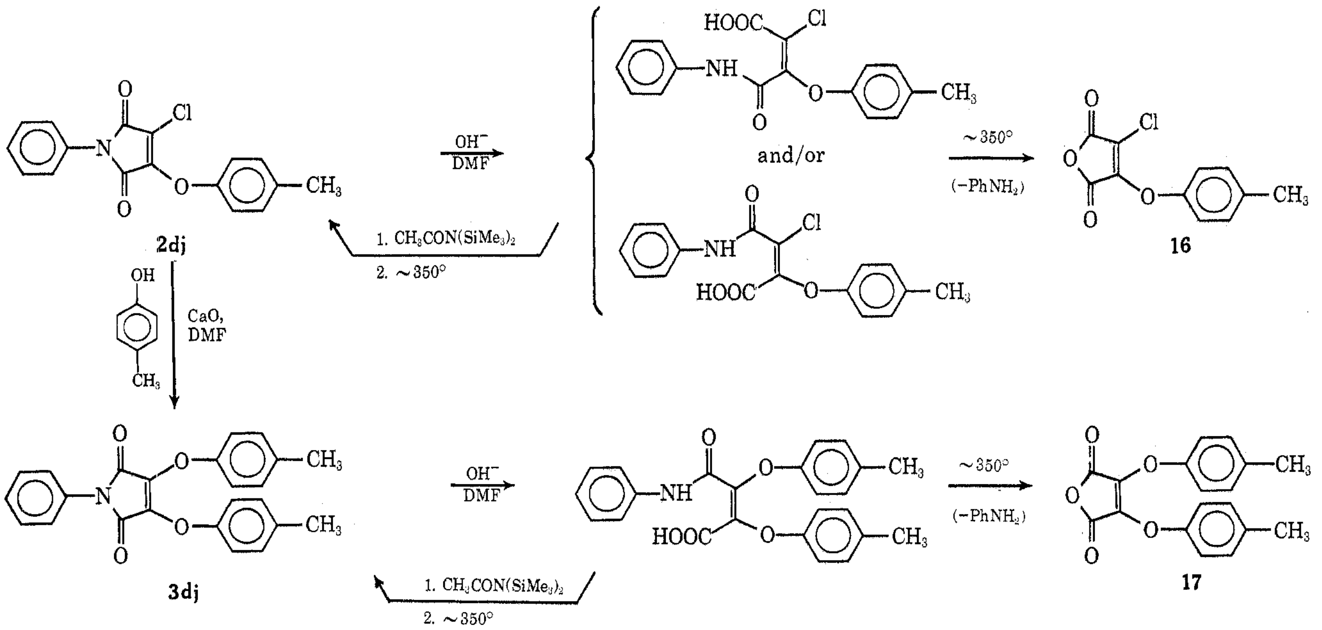
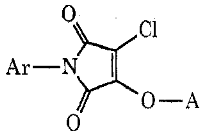


TABLE II

MASS SPECTRA[a] OF N-ARYL-3-ARYLOXY-4-CHLOROMALEIMIDES, 2



Compd	M^+	$(M - C_3ClO_2)^+$	$(M - OAr')^+$	$(M - C_4ClO_3)^+$	$(ArNCCl)^+$	$(ArNCO)^+$	$(OAr')^+$	$(C_3ClO_2)^+$
2aj	343 (100)	240 (41)	236 (21)	212 (62)	168 (19)	149 (21)	107 (20)	103 (43)
2bk	391 (100)	288 (18)	298 (3)	260 (38)	230 (7)	211 (23)	93 (2)	103 (36)
2cj	327 (100)	244 (87)	220 (50)	196 (75)	152 (40)	133 (29)	107 (45)	103 (124)
2di	329 (100)	226 (92)	206 (25)	198 (42)	138 (46)	119 (25)	123 (105)	103 (101)
2dj	313 (100)	210 (88)	206 (26)	182 (41)	138 (22)	119 (23)	107 (10)	103 (52)
2dk	299 (100)	196 (120)	206 (20)	168 (55)	138 (18)	119(22)	93 (7)	103 (52)
2dl	333 (100)[c]	230 (107)[b]	206 (63)	202 (42)[b]	138 (48)	119 (44)	127 (9)[b]	103 (143)
2dm	377 (100)[d]	274 (129)[e]	206 (51)	246 (7)[e]	138 (51)	119 (83)	171 (1)[e]	103 (170)
2dn	324 (100)	221 (170)	206 (23)	193 (87)	138 (33)	119 (77)	118 (2)	103 (176)
2dp	327 (100)	224 (14)	206 (16)	196 (4)	138 (23)	119 (38)	121 (13)	103 (98)
2ej	347 (100)[c]	224 (76)[b]	240 (19)[c]	216 (49)[b]	172 (23)[c]	153 (23)[b]	107 (22)	103 (154)
2fi	363 (100)[c]	260 (8)[b]	240 (10)[c]	232 (24)[b]	172 (25)[c]	153 (17)[b]	123 (163)	103 (168)
2fk	333 (100)[c]	230 (142)[b]	240 (17)[c]	202 (34)[b]	172 (20)[c]	153 (39)[b]	93 (7)	103 (172)
2fl	367 (100)[f]	264 (100)[c]	240 (57)[c]	236 (28)[c]	172 (47)[c]	153 (51)[b]	127 (24)[b]	103 (321)
2fm	411 (100)[g]	308 (119)[d]	240 (39)[c]		172 (44)[c]	153 (101)[b]		103 (395)
2gj	338 (100)	235 (75)	231 (7)	207 (56)	163 (9)	144 (8)	107 (9)	103 (101)
2hj	341 (100)	238 (15)	234 (58)	210 (15)	166 (22)	147 (8)	107 (15)	103 (54)
2hp	355 (100)	252 (1)	234 (22)		166 (13)	147 (12)	121 (151)	103 (86)

[a] m/e (and relative intensity) given. Unless otherwise indicated, the $(M)^+$, $(M - OAr)^+$, $(ArNCCl)^+$, and $(C_3ClO_2)^+$ ions occurred as one-chlorine clusters. Many peaks were present with m/e less than 93 but were omitted from this tabulation. Some significant peaks, other than those tabulated, were also observed: **2aj**, 134 (36); **2bk**, 167 (31); **2cj**, 119 (25), 132 (45), 181 (28); **2di**, 228 (25); **2dj**, 167 (15); **2dl**, 111 (118),[b] 123 (33),[b] 139 (37),[b] 167 (57), 178 (16);[b] **2dm**, 155 (92),[e] 167 (158), 178 (29),[b] 183 (22);[e] **2dn**, 102 (174), 114 (38), 130 (37); **2dp**, 292 (91); **2ej**, 119 (36), 125 (30), 181 (42); **2fi**, 226 (69);[b] **2fk**, 167 (51); **2fl**, 111 (283),[b] 123 (59),[b] 125 (37),[b] 139 (57),[b] 201 (81);[b] **2fm**, 155 (201),[e] 201 (168);[b] **2gj**, 119 (16), 192 (18), 210 (22);[b] **2hj**, 221 (39); **2hp**, 208 (43),[b] 320 (122). [b] One-chlorine cluster. [c] Two-chlorine cluster. [d] One-chlorine, one-bromine cluster. [e] One-bromine cluster. [f] Three-chlorine cluster. [g] Two-chlorine, one-bromine cluster.

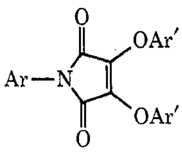
in 40 ml of chlorobenzene being stirred in a nitrogen atmosphere. Water was completely removed by azeotropic distillation and subsequent passage of the refluxing liquid through a calcium hydride bed. The system was then cooled to ~25°.

To the resulting suspension of 0.020 mol of sodium 4-methylphenoxide was added 2.72 g (0.010 mol) of N-(4-methoxyphenyl)-3,4-dichloromaleimide, **1a**, 20 ml of anhydrous chlorobenzene, and 6 ml of anhydrous dimethyl sulfoxide (DMSO). The solution rapidly became homogeneous and, after it was stirred at ~25° for 1.5 hr, it was added to 100 ml of chloroform and extracted several times with 1 N HCl (to remove the DMSO), dried ($MgSO_4$), and freed of solvent *in vacuo*. The solid residue, which also contained a small amount of chlorobenzene, was recrystallized from hexane. There was obtained 3.60 g (87%) of **3aj**: mp 166–167°; ^1H nmr spectrum δ 6.53–7.36 (m, 12, aromatic), 3.68 (s, 3, OCH_3), and 2.20 (s, 6, CH_3Ar); ir strong C=O with fine structure maxima at 1690, 1710, and 1720 cm^{-1} (*no peak* at all near 1650 cm^{-1}); for mass spectrum see Table III.

N-(4-Phenoxyphenyl)-3-phenoxy-4-chloromaleimide, 2bk.—N,N-Dimethylformamide (DMF, 50 ml) was added to 3.34 g (0.010 mol) of N-(4-phenoxyphenyl)-3,4-dichloromaleimide, **1b**, and 0.94 g (0.010 mol) of phenol. To the resulting solution was

TABLE III

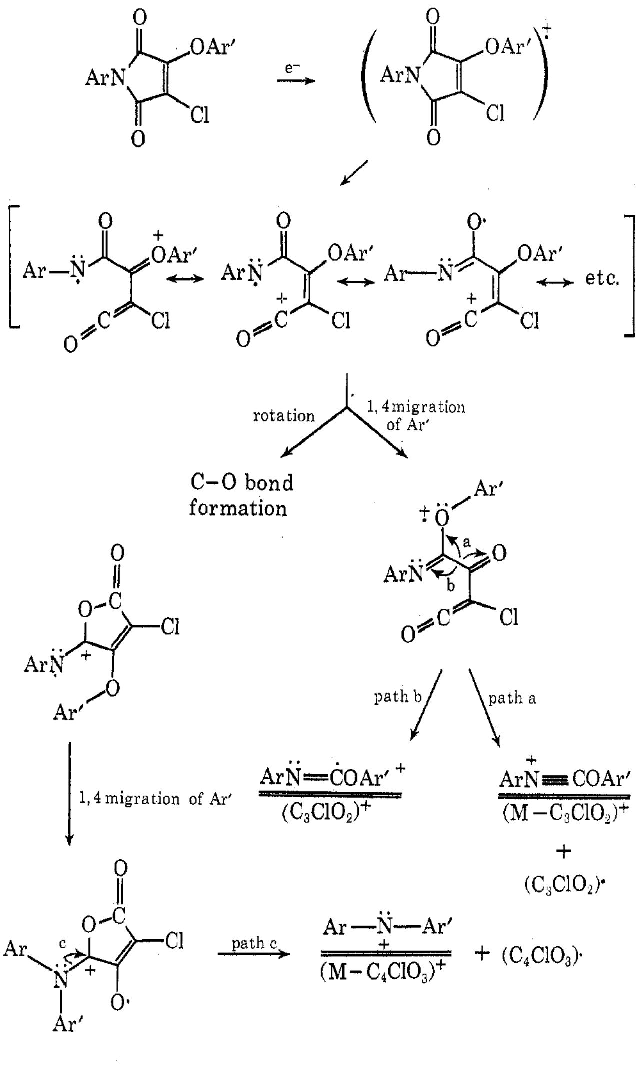
MASS SPECTRA[a] OF *N*-ARYL-3,4-DIARYLOXYMALEIMIDES, 3



Compd	M$^+$	(M − C_3O_3Ar')$^+$	(M − OAr′)$^+$	(M − C_4O_4Ar')$^+$	(ArNCO)$^+$	(OAr′)$^+$	(C_3O_3Ar')$^+$
3aj	415 (100)	240 (29)	308 (1)	212 (59)	149 (57)	107 (147)	175 (35)
3dj	385 (100)	210 (27)	278 (3)	182 (19)	119 (66)	107 (58)	175 (30)
3dk	357 (100)	196 (41)	264 (2)	168 (22)	119 (15)	93 (43)	161 (19)
3hj	413 (100)	238 (21)	306 (14)	210 (4)	147 (24)	107 (102)	175 (67)

[a] *m/e* (and relative intensity) are given. Some significant peaks, other than those tabulated, were also observed: **3aj**, 252 (39), 224 (28), 134 (73), 119 (140); **3dj**, 222 (28); **3dk**, 331 (49), 239 (36), 238 (50), 208 (32); 105 (53); **3hj**, 278 (21), 262 (19), 221 (24), 132 (26), 119 (215).

SCHEME IV



added 6.91 g (0.05 mol) of anhydrous K_2CO_3 and stirring was maintained for 3 hr at ~25°. Chloroform was added, the excess K_2CO_3 was filtered off, and the filtrate was extracted with 1 *N* HCl (to remove DMF) and dried over $MgSO_4$. Solvent removal and recrystallization of the product from carbon tetrachloride gave 2.5 g (64%) of **2bk**, mp 146–148°. Another recrystallization from chloroform afforded an analytical sample: mp 148.5–149°; ir 1649 and 1722 cm^{-1} (two C═O); for mass spectrum see Table II.

Anal. Calcd for $C_{22}H_{14}ClNO_4$: C, 67.5; H, 3.6; N, 3.6; Cl, 9.1. Found: C, 67.3; H, 3.6; N, 3.5; Cl, 9.1.

N-**(4-Methylphenyl)-3-(4-methylphenoxy)-4-chloromaleimide, 2cj.**—A solution of 5.12 g (0.020 mol) of *N*-(4-methylphenyl)-3,4-dichloromaleimide, **1c**, and 2.16 g (0.020 mol) of 4-methylphenol in 50 ml of methylene chloride was stirred with 13.8 g (0.10 mol) of anhydrous K_2CO_3 in dry air, at ~25°, for 7 days. The reaction mixture was cautiously (CO_2 evolution) added to a stirred mixture of 250 ml of chloroform and 250 ml of 1 *N* HCl. The layers were separated; the organic layer was extracted with water, dried ($MgSO_4$), and freed of solvent *in vacuo* to give 6.40 g of a solid product. Recrystallization from ethanol afforded 5.78 g (88%) of **2cj**: mp 166–167°; ^{1}H nmr spectrum δ 2.33 (slightly broadened singlet, 6, two CH_3's), 6.90–7.40 (m, 8, aromatic); ir 1650 and 1723 cm^{-1} (two C═O); for mass spectrum see Table II.

N-**Phenyl-3-(4-methoxyphenoxy)-4-chloromaleimide, 2di.**—A solution of 4.84 g (0.020 mol) of *N*-phenyl-3,4-dichloromaleimide, **1d**, and 2.48 g (0.020 mol) of 4-methoxyphenol in 50 ml of methylene chloride was stirred at ~25° for 20 hr with 13.8 g (0.10 mol) of anhydrous K_2CO_3. Work-up and recrystallization, as described above for **2cj**, afforded 5.79 g (88%) of **2di**: mp 130.5–131.5°; ^{1}H nmr spectrum δ 3.66 (s, 3, OCH_3), 6.54–7.36 (m, 9, aromatic); ir 1653 and 1726 cm^{-1} (two C═O); for mass spectrum see Table II.

N-**Phenyl-3-(4-methylphenoxy)-4-chloromaleimide, 2dj.**—Exactly 24.21 g (0.100 mol) of *N*-phenyl-3,4-dichloromaleimide, **1d**, and 10.81 g (0.100 mol) of 4-methylphenol were stirred in 250 ml of methylene chloride with 69.1 g (0.50 mol) of anhydrous K_2CO_3 at ~25° for 3 days. [After only 2 days, vapor phase chromatographic (vpc) analysis showed that all of the starting materials were absent and only **2dj** was present.] The system was then carefully added to 1 l. of 1 *N* HCl and 750 ml of methylene chloride. The organic phase was separated, extracted with water, dried, and freed of solvent in vacuo. The pale yellow solid (29.8 g) obtained was recrystallized from hexane to give 25.3 g (81%) of pure **2dj**: mp 102–103°; ^{1}H nmr spectrum (CH_2Cl_2) δ 6.8–7.5 (m, 9, aromatic), 2.27 (s, 3, CH_3); ir ($HCCl_3$) 1653 and 1730 cm^{-1} (two C═O); for ^{13}C nmr spectrum and mass spectrum see Tables I and II, respectively.

Anal. Calcd for $C_{17}H_{12}ClNO_3$: C, 65.0; H, 3.9; Cl, 11.3. Found: C, 64.7; H, 3.9; Cl, 11.4.

N-**Phenyl-3-phenoxy-4-chloromaleimide, 2dk.**—This material was prepared from **1d** and phenol by the method used for **2cj** except that the reaction time was only 20 hr. Recrystallization, as in the case of **2cj**, afforded 4.52 g (76%) of **2dk**: mp 132.5–133.5°; ir 1653 and 1725 cm^{-1} (two C═O); for ^{13}C nmr spectrum and mass spectrum see Tables I and II, respectively.

Anal. Calcd for $C_{16}H_{10}ClNO_3$: Cl, 11.8. Found: Cl, 11.8.

N-**Phenyl-3-(4-chlorophenoxy)-4-chloromaleimide, 2dl.**—This material was prepared from **1d** and 4-chlorophenol and recrystallized by the method described for **2cj** except that the reaction time was 20 hr. The yield was 5.86 g (88%): mp 139–141°; ir 1643 and 1728 cm^{-1} (two C═O); for mass spectrum see Table II.

Anal. Calcd for $C_{16}H_9Cl_2NO_3$: Cl, 21.2. Found: Cl, 21.5.

N-**Phenyl-3-(3-bromophenoxy)-4-chloromaleimide, 2dm.**—Preparation of this material from **1d** and 3-bromophenol and recrystallization were carried out using the method described for **2cj** except that the reaction time was 20 hr. There was obtained 5.50 g (73%) of **2dm**: mp 115–116.5°; ir 1657 and 1727 cm^{-1} (two C═O); for mass spectrum see Table II.

Anal. Calcd for $C_{16}H_9BrClNO_3$: C, 50.7; H, 2.4; N, 3.7. Found: C, 50.4; H, 2.6; N, 3.9.

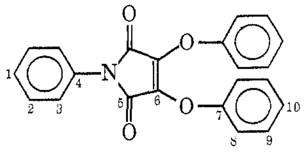
N-**Phenyl-3-(4-cyanophenoxy)-4-chloromaleimide, 2dn.**—This material was prepared from **1d** and 4-cyanophenol and recrystallized as described for **2cj** except that the reaction was carried out for 11 days. (After 6 days, vpc analysis showed that the reaction was not yet complete.) The amount of **2dn** obtained was 5.54 g (86%): mp 161–163°; ir 1652 and 1730 cm^{-1} (two C═O), 2235 cm^{-1} (C≡N); for mass spectrum see Table II.

Anal. Calcd for $C_{17}H_9ClN_2O_3$: Cl, 10.9. Found: Cl, 10.9.

***N*-Phenyl-3,4-bis(4-methylphenoxy)maleimide, 3dj.**—To an anhydrous solution of 0.0212 mol of sodium 4-methylphenoxide in 40 ml of DMSO and 20 ml of chlorobenzene, prepared in a manner analogous to that used during the preparation of **3aj**, was added 2.567 g (0.0106 mol) of *N*-phenyl-3,4-dichloromaleimide, **1d.** Vpc analysis showed that the reaction was complete in less than 20 min; only **3dj** was present; **1d** and **2dj** were absent. Chloroform was added and the mixture was extracted with 1 *N* HCl until no more DMSO remained (according to nmr analysis), dried, and freed of solvent in *vacuo*. The product thus obtained (8.1 g) was essentially pure **3dj**: ^{1}H nmr spectrum δ 6.5–7.5 (m, 13, aromatic), 2.22 (s, 6, CH_3). Recrystallization from cyclohexane afforded an analytical sample: mp 171–172°; ir strong C═O with fine structure maxima at 1686 and 1723 cm^{-1} (no bands were present in the 1650-cm^{-1} region); for mass spectrum see Table III.

Anal. Calcd for $C_{24}H_{19}NO_4$: C, 74.8; H, 4.9; N, 3.6. Found: C, 75.2; H, 5.0; N, 3.9.

***N*-Phenyl-3,4-bis(phenoxy)maleimide, 3dk.**—While a solution of 2.42 g (0.0100 mol) of **1d** in 25 ml of anhydrous DMSO was being stirred in a nitrogen glove box, 2.32 g (0.0200 mol) of anhydrous sodium phenoxide was added in small portions so as to maintain the reaction temperature below 50° (25 min). A chloroform/water work-up afforded 3.5 g of a yellow solid which, after recrystallization from cyclohexane/benzene, gave 2.70 g (76%) of **3dk**: mp 165.5–166°; ir 1700 and 1728 cm^{-1} (C═O); for mass spectrum see Table III. The ^{13}C nmr spectrum (acetone-d_6) was in accord with the assigned structure (C_n designations from **18** and chemical shift in parts per million): C_1, 128.4; C_2, 129.6; C_3, 127.3; C_4, 132.4; C_5, 164.8; C_6, 134.6; C_7, 156.1; C_8, 118.0; C_9, 130.2; C_{10}, 125.1.



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Anal. Calcd for $C_{22}H_{15}NO_4$: C, 73.9; H, 4.2; N, 3.9. Found: C, 74.2; H, 4.4; N, 4.2.

***N*-(4-Chlorophenyl)-3-(4-methylphenoxy)-4-chloromaleimide, 2ej.**—A solution of 1.66 g (0.0060 mol) of *N*-(4-chlorophenyl)-3,4-dichloromaleimide, **1e**, and 0.65 g (0.0060 mol) of 4-methylphenol in 15 ml of methylene chloride was stirred at ~25° for 47 hr with 4.15 g (0.030 mol) of anhydrous K_2CO_3. Work-up and recrystallization were carried out, as described for **2cj**, to give 1.68 g (81%) of **2ej**: mp 156.5–157.5°; ir 1648 and 1727 cm^{-1} (two C═O); ^{1}H nmr spectrum δ 6.90–7.60 (m, 8, aromatic), 2.40 (s, 3, CH_3); for mass spectrum see Table II; for ^{13}C nmr spectrum see Table I.

***N*-(3-Chlorophenyl)-3-(4-methoxyphenoxy)-4-chloromaleimide, 2fi.**—The preparation of this material from **1f** and 4-methoxyphenol and its purification were carried out as described for **2cj** except that the reaction was run on a 0.030 mol scale for 41 hr. The yield of **2fi** was 9.8 g (90%): mp 119–120°; ir 1648 and 1727 cm^{-1} (two C═O); for mass spectrum see Table II; ^{1}H nmr spectrum δ 6.6–7.4 (m, 8, aromatic), 3.70 (s, 3, OCH_3).

***N*-(3-Chlorophenyl)-3-phenoxy-4-chloromaleimide, 2fk.**—This material was prepared from **1f** and phenol and recrystallized by the method described for **2cj** except that the scale was 0.015 mol and the reaction time was 25 hr. The yield of **2fk** was 3.36 g (67%): mp 98–99°; ir 1651 and 1730 cm^{-1} (two C═O); for mass spectrum see Table II.

Anal. Calcd for $C_{16}H_9Cl_2NO_3$: Cl, 21.2. Found: Cl, 21.6.

***N*-(3-Chlorophenyl)-3-(4-chlorophenoxy)-4-chloromaleimide, 2fl.**—Using the method described for the preparation and purification of **2cj**, **2fl** was prepared in a 0.0154 mol scale reaction (reaction time of 22 hr) from **1f** and 4-chlorophenol. The yield of **2fl** was 3.73 g (66%): mp 124.5–125.5°; ir 1648 and 1731 cm^{-1} (two C═O); for mass spectrum see Table II.

Anal. Calcd for $C_{16}H_8Cl_3NO_3$: Cl, 28.8. Found: Cl, 28.8.

***N*-(3-Chlorophenyl)-3-(3-bromophenoxy)-4-chloromaleimide, 2fm.**—This material was prepared from **1f** and 3-bromophenol and recrystallized as described for **2cj** except that the reaction time was 25 hr and the scale was 0.015 mol. The yield of **2fm** was 4.61 g (74%): mp 116.5–118.5°; ir 1654 and 1723 cm^{-1} (two C═O); for mass spectrum see Table II.

Anal. Calcd for $C_{16}H_8BrCl_2NO_3$: C, 46.5; H, 1.93; N, 3.4. Found: C, 46.2; H, 2.04; N, 3.6.

***N*-(4-Cyanophenyl)-3-(4-methylphenoxy)-4-chloromaleimide, 2gj.**—A solution of 0.450 g (0.0017 mol) of *N*-(4-cyanophenyl)-3,4-dichloromaleimide, **1g**, and 0.184 g (0.0017 mol) of 4-methylphenol in 4.5 ml of anhydrous *N*,*N*-dimethylformamide (DMF) was stirred with 0.180 g (0.0017 mol) of anhydrous, powdered Na_2CO_3 at ~25° for 100 min. The entire system was added to 10 ml of chloroform and 10 ml of 1 *N* HCl and, after the layers were shaken, the aqueous layer was discarded. The chloroform layer was extracted four more times with 15-ml portions of 1 *N* HCl, dried ($MgSO_4$), and freed of solvent *in vacuo*. The solid product (0.58 g), after recrystallization from EtOH, gave 0.36 g (63%) of **2gj**: mp 190–191.5°; ir 1648 and 1728 cm^{-1} (two C═O), 2235 cm^{-1} (C≡N); ^{1}H nmr spectrum (DMSO-d_6) δ 7.2–8.2 (m, 8, aromatic), 2.32 (s, 3, CH_3); for mass spectrum see Table II; for ^{13}C nmr spectrum see Table I.

***N*-(2,6-Dimethylphenyl)-3-(4-methylphenoxy)-4-chloromaleimide, 2hj.**—This material was prepared from **1h** and 4-methylphenol and purified by the method described for the preparation of **2cj** except that the reaction time was only 47 hr. The yield of **2hj** was 5.89 g (86%): mp 151.5–152.5°; ir 1653 and 1723 cm^{-1} (two C═O); ^{1}H nmr spectrum δ 6.95–7.33 (m, 7, aromatic), 2.17 (s, 6, CH_3's on the *N*-aryl ring), 2.36 (s, 3, CH_3 on the *O*-aryl ring); for mass spectrum see Table II.

***N*-(2,6-Dimethylphenyl)-3-(2,6-dimethylphenoxy)-4-chloromaleimide, 2hp.**—Exactly 5.40 g (0.020 mol) of *N*-(2,6-dimethylphenyl)-3,4-dichloromaleimide, **1h**, and 2.44 g (0.020 mol) of 2,6-dimethylphenol in 50 ml of anhydrous DMF were stirred at ~25° for 5 hr with 10.6 g (0.10 mol) of anhydrous, powdered Na_2CO_3. Work-up, similar to that used in the preparation of **2gj**, gave 6.56 g of crude product which, after recrystallization from EtOH, gave 5.39 g (76%) of **2hp**: mp 157.5–158.5°; ir 1650 and 1725 cm^{-1} (two C═O); ^{1}H nmr spectrum δ 7.00–7.35 (m, 6, aromatic), 2.18 (s, 6, CH_3's on the *N*-aryl ring), 2.32 (s, 6, CH_3's on the *O*-aryl ring); for mass spectrum see Table II.

***N*-(2,6-Dimethylphenyl)-3,4-bis(4-methylphenoxy)maleimide, 3hj.**—Exactly 0.01801 mol of anhydrous sodium 4-methylphenoxide was prepared, as described in the preparation of **3aj**, in 35 ml of DMSO and 35 ml of chlorobenzene. To this solution under nitrogen was added 2.43 g (0.00900 mol) of **1h** and, after 1.5 hr, work-up was affected as described for **3aj**. Recrystallization from hexane afforded 2.24 g (60%) of **3hj**: mp 128–129.5°; ir 1690 and 1720 cm^{-1} (C═O); ^{1}H nmr spectrum δ 6.5–7.1 (m, 11, aromatic), and two very nearly coincident singlets, for the *N*-aryl ring methyls and the *O*-aryl ring methyls, both at 2.17 δ (total 12 H); for mass spectrum see Table III.

***N*-Methyl-3-(4-methylphenoxy)-4-chloromaleimide, 4.**—This material was prepared from *N*-methyl-3,4-dichloromaleimide and 4-methylphenol by the method used for the synthesis of **2cj** except that the reaction time was only 47 hr. After recrystallization, there was obtained 3.93 g (78%) of **4**: mp 111–112°; ir 1652 and 1723 cm^{-1} (two C═O); ^{1}H nmr spectrum δ 6.90–7.35 (m, 4, aromatic), 3.04 (s, 3, N-CH_3), 2.36 (s, 3, CH_3Ar); mass spectrum *m/e* [rel intensity, probable assignment given] 251 [100, one-chlorine molecular ion cluster], 148 [3, $(M - C_3ClO_2)^+$], 147 [10, $(M - C_3ClO_2 - H)^+$], 144 [17, $(M - OAr)^+$ one-chlorine cluster], 120 [5, $(M - C_4ClO_3)^+$], 119 [20, $(M - C_4ClO_3 - H)^+$], 107 [12, OAr^+] 103 [101, $(C_3ClO_2)^+$ one-chlorine cluster].

The Reaction of 1d with 2,6-Dimethylphenol. A. Preparation of *N*-Phenyl-3-(2,6-dimethylphenoxy)-4-chloromaleimide, 2dp.—To a solution of 4.84 g (0.02 mol) of **1d** and 2.44 g (0.02 mol) of 2,6-dimethylphenol in 50 ml of anhydrous DMF was added 10.6 g (0.1 mol) of anhydrous Na_2CO_3. The system was stirred at ~25° for 5 hr, combined with 50 ml of chloroform, and then extracted with six 100-ml portions of 1 *N* HCl. The crude product was isolated by drying the chloroform solution with $MgSO_4$ and removing the solvent *in vacuo*. (It was completely soluble in ethanol, a fact which indicates the total absence of **5**; see expt B below.) Recrystallization from 75 ml of cyclohexane gave 3.6 g of **2dp**: mp 88–89°; ^{1}H nmr spectrum δ 2.33 (s, 6, CH_3), 7.25–7.59 (m, 8, aromatic); ir 1649 and 1728 cm^{-1} (two C═O); for mass spectrum see Table II.

Anal. Calcd for $C_{18}H_{14}ClNO_3$: Cl, 10.84. Found: Cl, 11.2.

B. **Preparation of *N*-Phenyl-3-(2,6-dimethylphenoxy)-4-chloromaleimide, 2dp, and *N*-Phenyl-3-{2,6-dimethyl-4-[3-(*N*-phenyl-4-chloro)maleimido]phenoxy}-4-chloromaleimide, 5.**—A solution of 4.84 g (0.02 mol) of **1d** and 2.44 g (0.02 mol) of 2,6-dimethylphenol in 50 ml of methylene chloride was stirred at ~25° with 13.8 g (0.10 mol) anhydrous K_2CO_3. After 6 days, vpc analysis showed that much of the starting materials remained and that only one volatile product, R_t = 9.7 min, had been produced. After 11 days, only a trace of **1d** was left, although a significant amount of 2,6-dimethylphenol remained; the material with R_t = 9.7 min was still the only volatile product observed. The system was then worked up as described for **2cj** and 7.19 g of crude product was obtained. This material was dissolved in 250 ml of EtOH and 100 ml of $HCCl_3$, concentrated to 200 ml by distillation, and then allowed to cool slowly to *ca.* 25°. The yellow crystalline material, which had separated, was filtered and dried. In this way, 1.31 g of a material, mp 208–211°, was obtained which subsequently proved to be **5**:[13] ir 1656, 1708, and 1722 cm^{-1} (C=O) (no -OH band); ^{1}H nmr spectrum δ 2.29 (slightly broadened singlet, 6, CH_3), 7.2–7.9 (m, 12, aromatic); mass spectrum *m/e* [rel intensity, assignment] 532 [100, two-chlorine molecular-ion cluster], 497 [55, $(M - Cl)^+$ one-chlorine cluster], 429 [5, $(M - C_3ClO_2)^+$ one-chlorine cluster], 413 [15, $(M - C_6H_5NCO)^+$ two-chlorine cluster], 378 [17, $(M - C_6H_5NCO\text{-}Cl)^+$ one-chlorine cluster], 326 [9, OAr^+ one-chlorine cluster], 310 [29, Ar^+ (from OAr portion) one-chlorine cluster], 206 [34, $(M - OAr)^+$ one-chlorine cluster], 119 [37, $(C_6H_5NCO)^+$], 103 [66, $(C_3ClO_2)^+$ one-chlorine cluster].

Anal. Calcd for $C_{28}H_{18}Cl_2N_2O_5$: Cl, 13.4. Found: Cl, 13.9.

Concentration of the above filtrate to 80 ml gave a second crop of 0.12 g of **5**; the total yield of **5** was 1.43 g (27%, based on **1d**).

Solvent removal from the second crop of **5** gave a viscous oil which could not be crystallized. Vpc and nmr analysis indicated that it was approximately a 1:4 mixture of 2,6-dimethylphenol and **2dp**. Indeed, a pure sample of the latter (R_t = 9.7 min) was isolated by preparative vpc and displayed the same mass spectrum as found previously for **2dp** (Table II).

Attempted Preparation of *N*-(3-Chlorophenyl)-3-(4-chlorophenoxy)-4-(4-methoxyphenoxy)maleimide, 15.—To a suspension of 0.0150 mol of anhydrous sodium 4-chlorophenoxide in 40 ml of chlorobenzene, prepared in a manner analogous to that described above for the preparation of sodium 4-methylphenoxide, was added 5.46 g (0.0150 mol) of **2fi** and 10 ml of anhydrous DMSO in a nitrogen atmosphere. The system rapidly became homogeneous. After the solution stirred for 1 hr at ~25°, it was worked up as described in the preparation of **3aj**. A total of 5.16 g of material (mp 94–100°) crystallized from the hexane–chlorobenzene solution. Thin layer chromatography (on silica, with benzene as solvent) indicated that this material contained at least three components. Several attempts at purification by recrystallization failed; each time there was obtained a broad melting mixture which showed an appropriate methoxy singlet (δ 3.72) and aromatic multiplet (δ 6.5–7.5) in the ^{1}H nmr spectrum in various ratios, all within ±15% of that expected for **15**. The three components of these mixtures were found by mass spectrometry to be **3fi**, **15**, and **3fl**; they displayed the appropriate one-, two-, and three-chlorine molecular-ion clusters, respectively (Table IV).

Other Reactions between 1d and 4-Methylphenol. I. Triethylamine in Methylene Chloride.[14]—A solution of 0.24 g (0.0010 mol) of **1d** and 0.43 g (0.0040 mol) of 4-methylphenol in 10 ml of methylene chloride was stirred at *ca.* 25° and 0.30 g (0.0030 mol) of triethylamine was added. Samples of the solution were taken at various times and analyzed by vpc (reaction time and mole ratio of **1d**:**2dj** given): 45 min, 2:98; 110 min, 0.3:99.7; no impurities were detected. A sample of the product was collected by preparative vpc and gave the same mass spectrum as found previously for **2dj** (Table II). The reaction mixture was extracted with 1 *N* HCl, 10% aqueous NaOH, and water, dried with $MgSO_4$, and freed of solvent *in vacuo*. The "crude" product (0.2 g) displayed ^{1}H nmr and infrared spectra which were superimposable on those obtained previously for **2dj**.

TABLE IV

PARTIAL MASS SPECTRUM[a] OF A MIXTURE OF **3fi**, **15**, AND **3fl**

m/e	Obsd rel intensity	Calcd rel intensities **3fi**[b]	**15**[c]	**3fl**[d]	Total[e]
451	100.0	100.0			100.0
452	27.6	27.7			27.7
453	34.8	36.9			36.9
454	12.9	9.5			9.5
455	211.0	1.6	209.4		211.0
456	59.1	0.2	55.5		55.7
457	145.4		143.2		143.2
458	37.5		36.6		36.6
459	50.4		27.4	23.0	50.4
460	12.9		6.5	5.8	12.3
461	22.4		1.0	22.9	23.9
462	5.7		0.1	5.7	5.8
463	7.2			7.9	7.9
464	1.5			1.9	1.9
465	0.8			1.0	1.0
466	0.2			0.2	0.2

[a] No peaks at all above 466 or between 450 and 444; no significant peaks between 443 and 321. [b] Calculated for $C_{24}H_{18}ClNO_5$ by setting the intensity of the 451 peak equal to 100.0. [c] Calculated for $C_{23}H_{15}Cl_2NO_5$ by setting the intensity of the 455 peak equal to 209.4 (the difference between the observed intensity and that calculated for this peak in the molecular-ion cluster of **3fi**). [d] Calculated for $C_{22}H_{12}Cl_3NO_4$ by setting the intensity of the 459 peak equal to 23.0 (the difference between the observed intensity and that calculated for this peak in the molecular-ion cluster of **15**). [e] Agrees within experimental error with the observed relative intensities.

II. Pyridine in Methylene Chloride.[14]—Using pyridine (0.0030 mol) in place of triethylamine in expt I gave the same results, but at a much slower rate according to vpc analysis (reaction time and mole ratio of **1d**:**2dj** given): 30 min, 56:44; 60 min, 35:65.

III. Calcium Oxide in DMF.[14] A.—A solution of 0.24 g (0.0010 mol) of **1d** and 0.054 g (0.00050 mol) of 4-methylphenol in 2.50 ml of anhydrous DMF was stirred at *ca.* 25° with 0.56 g (0.010 mol) of anhydrous, powdered CaO. Samples (0.25 ml) of the slurry were removed at various times and added to 5 ml of chloroform and 5 ml of 1 *N* HCl with vigorous stirring. The chloroform layer was separated, dried, and then analyzed by vpc (reaction time and mole ratio of **1d**:**2dj** given): 20 min, 96:4; 45 min, 90:10; 110 min, 72:28; 24 hr, 48:52 (theory for this experiment, 50:50). No other products were detected.

B.—A solution of 0.24 g (0.0010 mol) of **1d** and 0.216 g (0.0020 mol) of 4-methylphenol in 2.50 ml of anhydrous DMF was stirred at *ca.* 25° with 0.56 g (0.01 mol) of CaO. Approximately 0.25-ml aliquots were removed at various times and each was then treated and analyzed by vpc as described above (expt III, A). In this way, **16** and **17** were detected, isolated, and identified. A portion of each aliquot was further treated with bis(trimethylsilyl)acetamide and then analyzed again by vpc. The results are listed in Table V.

Structures **16** and **17** are in complete accord with their mass spectra (Tables VI and VII, respectively). ^{1}H nmr spectrum of **16** showed δ 7.2 (m, 4, aromatic), 2.3 (s, 3, CH_3).

C.—Reactions using 0.0010 or 0.0040 mol of 4-methylphenol gave results similar to those reported above (expt III, B).

IV. Potassium Carbonate in DMF.[14]—A solution of 0.968 g (0.0040 mol) of **1d** and 0.432 g (0.0040 mol) of 4-methylphenol in DMF (10.00 ml = total volume) was stirred at ~25° with 5.52 g (0.040 mol) of anhydrous K_2CO_3. As described above, the reaction was followed by vpc (reaction time and relative molar amounts of **16**:**1d**:**2dj**, respectively, given): 20 min, 0:24:76; 155 min, 0:0:100; 17.5 hr, 5:0:95. No other materials were detected.

V. Sodium Carbonate in DMF.[14]—This reaction was carried out as described in IV except that the base was 4.24 g (0.040 mol) of anhydrous Na_2CO_3: 20 min, 0:2:98; 155 min, 0:0:100; 17.5 hr, 3:0:97. No other materials were observed.

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[13] This material could not be eluted at 290° from the vpc columns used herein.

[14] Mole ratios given in this experiment were determined from vpc peak areas and so must be regarded in a qualitative and not quantitative sense (error ±10%). Although retention times for the material involved were quite reproducible and, therefore, useful for identification, in many cases samples of the components were collected by preparative vpc and identified further by their mass spectra.

TABLE V

APPROXIMATE MOLE RATIOS OF COMPOUNDS DETERMINED BY VPC ON EACH ALIQUOT[a]

Reaction time, min	Compounds[b]				
	16	**1d**	**17**	**2dj**	**3dj**
20	0 (0)	79 (82)	0 (0)	21 (18)	0 (0)
45	2 (0)	8 (4)	0 (0)	89 (95)	1 (1)
75[c]	59[d] (0)	0 (0)	9[d] (0)	16[d] (68)[d]	16 (23)[d]
110[c]	61 (0)	0 (0)	24 (0)	9 (68)	4 (20)
24[c]	61 (0)	0 (0)	30 (0)	5 (70)	1 (19)

[a] Values in parentheses are from the vpc of the aliquots after silylation with bis(trimethylsilyl)acetamide. [b] **2dj** and **3dj** were identified by comparing retention times with those of authentic materials and by isolating them by preparative vpc and comparing their mass spectra with those of the authentic materials. **16** and **17** were identified by similar isolation and examination of nmr and/or mass spectra (see Tables VI and VII, respectively); the observed retention times on the silicone column used were in agreement with the observed molecular weights (mass spectra) of **16** and **17**. Retention times (minutes) follow: **16**, 2.05; **1d**, 2.40; **17**, 6.30; **2dj**, 7.60; **3dj**, 12.40. [c] Unknown minor impurities were also present. [d] These were the samples collected and identified by their mass spectra.

TABLE VI

MASS SPECTRUM OF **16**

m/e	Rel intensity		Probable assignment
	Found	Calcd	
91	230.5		C_7H_7
103	274.0		One-chlorine cluster for C_3ClO_2; rearrangement ion[a]
105	82.7		
107	36.2		C_7H_7O
119	98.6		C_7H_7OC
134	46.3		C_7H_6OCO; rearrangement ion[a] −H
135	18.9		C_7H_7OCO; rearrangement ion[a]
147	24.7		C_7H_7OCCO; $M - C_2ClO_2$
210	21.6		One-chlorine cluster for $M - CO$
212	7.1		
238	100.0	100.0	Molecular-ion cluster: $C_{11}H_7ClO_4$
239	13.0	12.6	
240	33.3	33.5	
241	4.3	4.2	

[a] See discussion section for corresponding rearrangement ions in structurally similar imides **2** and **3**.

TABLE VII

MASS SPECTRUM OF **17**

m/e	Rel intensity		Probable assignment for ion
	Found	Calcd	
91	160.0		C_7H_7
107	104.0		C_7H_7O
119	54.0		C_7H_7OC
135	21.6		C_7H_7OCO; rearrangement ion[a]
147	18.8		C_7H_7OCCO
175	37.2		$C_7H_7OC_3O_2$; rearrangement ion[a]
310	100.0	100.0	Molecular-ion cluster: $C_{18}H_{14}O_5$
311	20.9	20.5	
312	3.1	3.0	
313	0.5	0.3	

[a] See footnote *a*, Table VI.

VI. Sodium Bicarbonate in DMF.[14]—This reaction was carried out as described in IV except that the base was 3.36 g (0.040 mol) of anhydrous $NaHCO_3$: 20 min, 0:99:1; 155 min, 0:55:45; 17.5 hr, 0:0:100. Carbon dioxide evolution was observed during this reaction. No other products were observed and, in particular, none of **16** was detected (vpc).

VII. Zinc Oxide in DMF.—This reaction was conducted as described in IV except that the base used was 3.34 g (0.040 mol) of anhydrous ZnO: 17.5 hr, 0:98:2 (very slow reaction).

VIII. Calcium Oxide in DMSO.—This experiment was performed as described in IV except that the solvent was anhydrous DMSO and the base was 2.24 g (0.040 mol) of anhydrous CaO: 20 min, 0:99:1; 155 min, 0:78:22; 31 hr, 0:0:100.

IX. Potassium Carbonate in DMSO.—This experiment was performed as described in IV except that the solvent was anhydrous DMSO: 20 min, 0:5:95; 155 min, 13:0:87.

X. Sodium Carbonate in DMSO.—This experiment was conducted as described in IV except that the solvent was anhydrous DMSO and the base was 4.24 g (0.040 mol) of anhydrous Na_2CO_3: 20 min, 1:0:99; 155 min, 8:0:92.

Registry No.—**1d**, 3876-05-9; **1h**, 35740-43-3; **2aj**, 35740-44-4; **2bk**, 35740-45-5; **2cj**, 35740-46-6; **2di**, 35740-47-7; **2dj**, 35740-48-8; **2dk**, 35740-49-9; **2dl**, 35740-50-2; **2dm**, 35740-51-3; **2dn**, 35740-52-4; **2dp**, 35740-53-5; **2ej**, 35740-54-6; **2fi**, 35740-55-7; **2fk**, 35740-56-8; **2fl**, 35820-77-0; **2fm**, 35740-57-9; **2gj**, 35820-78-1; **2hj**, 35740-58-0; **2hp**, 35740-59-1; **3aj**, 35740-60-4; **3dj**, 35740-61-5; **3dk**, 35740-62-6; **3hj**, 35740-63-7; **4**, 35740-64-8; **5**, 35740-65-9; **15**, 35740-66-0; **16**, 35740-67-1; **17**, 35740-68-2.

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