Table VI. Scavenger Experiment Results of the Decomposition of 6

$[CCl_3Br]$, M	0.0033	0.013	0.20	0.26	0.33	0.11	2.5
fraction of scavenged	0.14	0.49	0.58	0.71	0.95	0.95	0.96

determined by iodometry. The Freon solution was dried over anhydrous Na_2SO_4 and preserved at −78 °C.

Kinetic Measurements. The above-mentioned dilute Freon solutions (≲0.02 M) were sealed in glass tubes under high-purity N_2. A whole set of these tubes was placed in a thermostat (±0.05 °C), and they were taken out at specified times andd immediately frozen to dry ice temperature. The tubes were opened while cool, and the undecomposed peroxide titrated by standard iodometry.[24]

First-order rate constants at different temperatures and activation parameters were calculated by linear regression analysis. Values of rate constants and the standard deviations of determination are shown in Table IV. Results of the preliminary tests of rate–concentration relationships upon which the proper initial concentrations for kinetic determinations were chosen are given in Table V.

Decomposition Products of Diacyl Peroxides. The above-mentioned Freon-113 solutions (5–10 mL) of diacyl peroxides (0.14–0.56 M) were kept at room temperature for 2 days to allow complete decomposition; the resulting reaction mixtures were analyzed by GC. The main products, which in all cases corresponded to the coupling products of perfluoroalkyl radicals, were separated by preparative GC and identified by NMR and mass spectra. Yields of the coupling products are shown in Table II; they were determined by GC with the pure separated samples as calibration standards. Minor products (all below 5%) have not been identified, but from the information obtained by GC/MS, they appear to be products from halogen abstraction by perfluoroalkyl radicals.

$(CF^a_3CF^b_2CF^c_2)_2$: ^{19}F NMR δ 75.1 (a, 3 F), 116.6 (b, 2 F), 120.3 (c, 2 f); MS m/e 319 $[(M - F)^+]$, 269, 231, 219, 200, 181, 169, 150, 131, 119, 100, 69.

$(CF^a_3CF^b_2CF^c_2CF^d_2CF^d_2CF^d_2CF^d_2)_2$: ^{19}F NMR δ 81.9 (a, 3 F), 123.0 (b, 2 F), 124.0 (c, 2 F), 127.4 (d, 8 F).

$(HCF^a_2CF^b_2)_2$: ^{19}F NMR δ 142.0 (a, 2 F, d, J_{HF} = 54.0 Hz), 135.1 (b, 2 F); MS m/e 151 $[(M - CF_2H)^+]$, 132, 113, 101, 82, 69, 51.

$HCF^a_2CF^b_2CF^c_2CF^d_2)_2$: ^{19}F NMR δ 146.3 (a, 2 F, d, J_{HF} = 52.4 Hz), 133.3 (b, 2 F), 126.6 (c, 2 F), 125.2 (d, 2 F); MS m/e 332 $[(M - CF_3H)^+]$, 313, 295, 281, 263, 251, 243, 231, 220, 213, 201, 181, 169, 163, 151, 131, 119, 101, 100.

$(HCF^a_2CF^b_2CF^c_2CF^d_2CF^d_2)_2$: ^{19}F NMR δ 141.3 (a, 2 F, J_{HF} = 52.2 Hz), 133.4 (b, 2 F), 127.0 (c, 2 F), 125.3 (d, 6 F).

$[CF^a_3CF^b_2CF^c_2OCF^d(CF^e_3)_2]_2$: ^{19}F NMR δ 85.2 (a, 3 F), 134.2 (b, 2 F), 84.0 (c, 2 F), 143.3, 146.2, (d, 1 F), 80.3, 82.0 (e, 3 F); MS m/e 385 $[(M - C_3F_7O)^+]$, 297, 285, 263, 219, 200, 197, 169, 150, 147, 131, 119, 100, 97, 69.

$[(CF^a_3)_2CF^bOCF^c(CF^d_3)]_2$: ^{19}F NMR δ 82.7, 84.0 (a, 3 F), 143.8 (b, 1 F), 136.0, 136.8 (c, 1 F), 79.7, 80.9 (d, 3 F); MS m/e 551 $[(M - F)^+]$, 501, 385, 363, 335, 313, 297, 285, 219, 200, 197, 169, 150, 147, 131, 119, 100, 97, 69.

$(CF^a_3)_2CF^bCF^c(CF^d_3)OCF^e(CF^f_3)_2$: ^{19}F NMR δ 74.9 (a, 6 F), 186.6 (b, 1 F), 143.9 (c, 1 F), 79.9 (d, 3 F), 131.2 (e, 1 F), 83.2, 84.3 (f, 6 F); MS m/e 435 $[(M - F)^+]$, 385, 297, 285, 269, 247, 235, 219, 200, 197, 181, 161, 132, 119, 97.

$[(CF^a_3)_2CF^b]_2$: ^{19}F NMR δ[25] 74.7 (a, 6 F), 183.8 (b, 1 F); MS m/e 319 $[(M - F)^+]$, 250, 162, 150, 132, 124, 112, 74, 62.

Scavenger Experiment. The decomposition of peroxide 6 in 0.2 M Freon-113 solution was carried out at room temperature with the addition of various amounts of a scavenger, CCl_3Br. After the decomposition was completed, the amounts of the coupling products were determined by GC. The yields of coupling products diminish with the increase of the relative concentration of CCl_3Br and approach a constant value which corresponds to ~5% of the coupling products obtained without the addition of CCl_3Br. Typical results are shown in Table VI Scavenged product, $CF_3CF_2CF_2OCF(CF_3)Br$, was isolated and identified.

$CF^a_3CF^b_2CF^c_2OCF^d(CF^e_3)Br$: ^{19}F NMR δ 85.7 (a, 3 F), 133.8 (b, 2 F), 88.8 (c, 2 F, AB q, $\Delta\delta$ = 3.6 ppm, J_{AB} = 145 Hz), 80.8 (d, 1 F), 89.3 (e, 3 F).

Registry No. 1, 336-64-1; 2, 34434-27-0; 3, 21934-53-2; 4, 308-35-0; 5, 32687-76-6; 6, 56347-79-6; 7, 72836-49-8; n-C_3F_7COCl, 375-16-6; n-$C_7F_{15}COCl$, 335-64-8; HCF_2CF_2COCl, 663-73-0; $H(CF_2)_4COCl$, 376-71-6; $H(CF_2)_6COCl$, 41405-35-0; n-$C_3F_7OCF(CF_3)COF$, 2062-98-8; i-$C_3F_7OCF(CF_3)COF$, 10372-97-1; $(n\text{-}C_3F_7)_2$, 355-42-0; $(n\text{-}C_7F_5)_2$, 307-62-0; $(HCF_2CF_2)_2$, 377-36-6; $[H(CF_2)_4]_2$, 307-99-3; $[H(CF_2)_6]_2$, 865-84-9; $[n\text{-}C_3F_7OCF(CF_3)]_2$, 2501-01-1; $[i\text{-}C_3F_7OCF(CF_3)]_2$, 81219-02-5; i-$C_3F_7OCF(CF_3)CF(CF_3)_2$, 81219-03-6; $(i\text{-}C_3F_7)_2$, 354-96-1; $CF_3CF_2CF_2OCF(CF_3)Br$, 81219-04-7; perfluorobutanoic acid, 375-22-4; perfluorooctanoic acid, 335-67-1; 2,2,3,3-tetrafluoropropanoic acid, 756-09-2; 2,2,3,3,4,4,5,5-octafluoropentanoic acid, 376-72-7; 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanoic acid, 1546-95-8; perfluoropropylene oxide, 428-59-1; hexafluoroacetone, 684-16-2.

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Oxidation of Some 2-Methoxyphenols with Chlorous Acid

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Oxidation of 3-ethoxy-4-hydroxy-, 4-hydroxy-3-methoxy-5-methyl-, 3-chloro-4-hydroxy-5-methoxy-, and 2-hydroxy-3-methoxybenzaldehyde with chlorous acid gives, by oxidative aromatic ring cleavage between the oxygen-bearing carbon atoms, derivatives of (2*Z*,4*Z*)-2,4-hexadienedioic acid in low yields. Chlorous acid oxidation of 2-methoxyphenol and 3-hydroxy-4-methoxybenzaldehyde yields methoxy-1,4-benzoquinone and 5,5-dichloro-6,6-dihydroxy-2-methoxy-2-cyclohexene-1,4-dione, respectively. The hydrate as well as the corresponding methyl hemiacetal undergoes base-catalyzed ring contraction to a derivative of 1-hydroxy-4-oxo-2-cyclopentenecarboxylic acid. The kinetics of the ring contraction of the hydrate was investigated in aqueous solutions in the pH range 1.15–3.65, where the rearrangement appears to be subject to specific base catalysis.

Oxidative intradiol ring cleavage of 1,2-diphenols with formation of 2,4-hexadienedioic (muconic) acids is an important process in degradation of aromatic compounds by aerobic microorganisms.[2] Notably, the process plays a significant role in soil degradation of plant-produced phenolics, being thus a part of the carbon cycle of the

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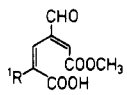
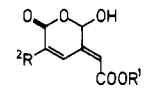
biosphere,[3] and in removal of man-made pollutants from the environment.[4] A limited number of reagents capable of chemically effecting similar transformations are available. At present, peroxy acids,[5] ozone,[6] and certain copper(II) complexes[7] seem to be most useful for preparation of 2,4-hexadienedioic acids directly[8] from aromatic precursors, although in all these cases the reaction scope is limited or unknown.

Oxidation of 4-hydroxy-3-methoxybenzaldehyde (vanillin, **1a**) with chlorous acid (acidified aqueous chlorite) has

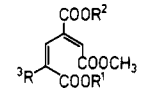
1 a $R^1 = CH_3$, $R^2 = OH$, $R^3 = R^4 = H$
b $R^1 = C_2H_5$, $R^2 = OH$, $R^3 = R^4 = H$
c $R^1 = CH_3$, $R^2 = OH$, $R^3 = CH_3$, $R^4 = H$
d $R^1 = CH_3$, $R^2 = OH$, $R^3 = Cl$, $R^4 = H$
e $R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = OH$
f $R^1 = H$, $R^2 = OCH_3$, $R^3 = R^4 = H$



2 a $R^1 = H$
b $R^1 = Cl$



3 a $R^1 = CH_3$, $R^2 = H$
b $R^1 = C_2H_5$, $R^2 = H$
c $R^1 = R^2 = CH_3$
d $R^1 = CH_3$, $R^2 = Cl$



4 a $R^1 = R^2 = R^3 = H$
b $R^1 = R^2 = H$, $R^3 = Cl$
c $R^1 = R^2 = CH_3$, $R^3 = Cl$
d $R^1 = CH_3$, $R^2 = R^3 = H$
e $R^1 = R^3 = H$, $R^2 = CH_3$

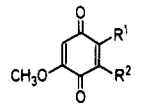
long been known to cause cleavage of the aromatic ring of the substrate to give **2a** (isolated as the cyclic hemiacetal **3a**) or **4a**, depending on the pH.[9-13] The former product was also obtained by oxidation of **1a** with chlorine dioxide at pH 4.[9,10,12] The yields of ring cleavage products amounted to 20–30%. Chlorine dioxide and chlorous acid[14] also cleaved the aromatic ring of (4-hydroxy-3-methoxyphenyl)methanol (vanillyl alcohol) in 7–17% yield.[15] In the few other instances reported, yields of products of aromatic ring cleavage with these reagents were negligible.[13,15,16]

Although it seems clear from earlier investigations that only monoethers of 1,2-diphenols are susceptible to production of 2,4-hexadienedioates with chlorous acid or chlorine dioxide[17] and that yields are slender, in the most favorable cases the reaction furnishes an easy access to unique, polyfunctional products (e.g., **3a** and **4a**) in one step. Therefore, it appeared appealing to us to examine oxidation with chlorous acid, the reagent of choice in laboratory practice, of some isomers and analogues of **1a** in order to check the generality of the reaction.

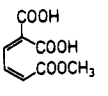
Results and Discussion

Following the first example,[9] the oxidations were carried out at low (pH 4, citrate–phosphate buffer) or high (pH 0.5, sulfuric acid) ratios of chlorous acid (pK_a ca. 2.0[14]) to chlorite, adding 4 molar equiv of the oxidant as sodium chlorite. Only products extractable with ether were analyzed. Oxidation of **1a** at pH 4 afforded 19–22% of **3a** (prepared in 7–8-g lots),[9] only small amounts of **4a** being formed. The latter was the sole product obtained at pH 0.5.[9] 3-Ethoxy-4-hydroxybenzaldehyde (ethyl vanillin, **1b**) and 4-hydroxy-3-methoxy-5-methylbenzaldehyde (**1c**) gave at pH 4 **3b** (17%) and **3c** (6%), respectively. Under these conditions 3-chloro-4-hydroxy-5-methoxybenzaldehyde (**1d**) was apparently unreactive, but at pH 0.5 a small amount of **3d** (2%) and **4b** (isolated as the trimethyl ester **4c**) together with a trace of **5a** was obtained.[18]

Oxidation of 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin, **1e**) gave at pH 4 a mixture of **5b** and **6**, the latter



5 a $R^1 = R^2 = Cl$
b $R^1 = H$, $R^2 = Cl$
c $R^1 = R^2 = H$
d $R^1 = Cl$, $R^2 = H$
e $R^1 = Cl$, $R^2 = OH$
f $R^1 = Cl$, $R^2 = OCH_3$



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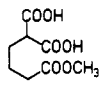

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being the sole product isolated at pH 0.5 (yield 7%). Catalytic hydrogenation of **6** gave **7**, which on being heated decarboxylated to monomethyl hexanedioate. Further

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(8) (a) After conversion of 1,2-diphenols to 1,2-benzoquinones, the latter can be cleaved to dialkyl 2,4-hexadienedioates with lead(IV) acetate[8b] or converted to cyclic anhydrides of 2,4-hexadienedioic acids with peroxy acids.[8c] (b) Wiessler, M. *Tetrahedron Lett.* **1977**, 233. Jaroszewski, J. W.; Ettlinger, M. G. *J. Org. Chem.*, in press. (c) Demmin, T. R.; Rogič, M. M. *Ibid.* **1980**, *45*, 1153.
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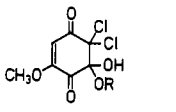
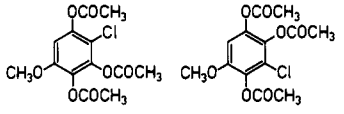
(17) (a) 1,2-Diphenols are very rapidly degraded apparently via 1,2-benzoquinones,[13,17b,c] whereas 1,2-dimethoxybenzenes are much more resistant toward these reagents, and no specific ring fission apparently takes place.[16,17c,d] Monophenols lacking an *o*-alkoxy substituent yield mainly chlorophenols and quinonoid products.[14,17e] (b) Glabisz, U. *Chem. Stosow., Ser. A* **1966**, *10*, 221. (c) Logan, C. D.; Husband, R. M.; Purves, C. B. *Can. J. Chem.* **1955**, *33*, 82. (d) Gianola, G.; Meybeck, J. *Bull. Assoc. Tech. Ind. Papet.* **1960**, 25. (e) Lindgren, B. O.; Ericsson, B. *Acta Chem. Scand.* **1969**, *23*, 3451. (f) See also: Strumila, G. B.; Rapson, W. H. *Trans. Tech. Sect., (Can. Pulp Pap. Assoc.)* **1977**, *3*, TR119.
(18) It cannot be said with certainty whether **5a** was formed from **1d** during the oxidation or was introduced into the reaction mixture as an impurity of **1d**.

investigations of **6** and its derivatives are reported elsewhere.[19]

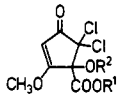
In contrast to the above examples, no ring cleavage was observed during oxidation of 2-methoxyphenol and 3-hydroxy-4-methoxybenzaldehyde (isovanillin, **1f**), the products obtained at pH 0.5 being, respectively, **5c** and **8a**. The structure of the latter product, aside from what was indicated by spectral properties, was inferred from its reductive acetylation to give **9**, which was also obtained by Thiele–Winter acetoxylation[20] of 2-chloro-5-methoxy-1,4-benzoquinone (**5d**). The triacetate **9** was further converted by acid-catalyzed methanolysis and mild oxidation to **5e**, which was methylated to give the previously described[21] quinone **5f**. The isomeric triacetate **10** was obtained by Thiele–Winter acetoxylation of **5b**.[22] The positions of the geminal chlorine atoms and hydroxy groups in **8a** are hence proved.



8 *a* R = H
b R = CH_3



9 **10**



11 *a* $R^1 = R^2 = H$
b $R^1 = CH_3$, $R^2 = H$
c $R^1 = H$, $R^2 = COCH_3$

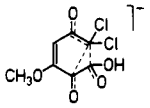
On heating in methanol, the hydrate **8a** was quantitatively converted into the hemiacetal **8b**. Both the hydrate and the hemiacetal, when treated with base, underwent rapid rearrangements to the respective cyclopentenones **11a** and **11b**. The pseudo-first-order rates of the conversion of **8a** to **11a** were measured by following the increase of ultraviolet absorption at 255 nm (λ_{max} of **11a**) in glycine buffers at 33 °C in the pH range 1.15–3.65 (Table I). In the pH range 1.65–3.30, where the rates could be measured most precisely, the data adhere to the equation $\log k = 0.96\ pH - 5.22$ (correlation coefficient 0.9998). The rates were apparently independent of buffer concentration and tended to increase with the ionic strength.

The ring contraction of **8a** and **8b** belongs to the class of anionotropic rearrangements of which the benzilic acid rearrangement[23] is the most familiar example. The rearrangement of **8a** and **8b** is particularly facile and occurs at appreciable rates even in fairly acidic solutions, presumably owing to effective charge delocalization in the transition state. Other examples of such ring contractions of hydrates of halogenated 1,2-diketones derived from cyclohexane have been recorded, most of them in the early literature.[24,25] From the data in Table I, a mechanism may be proposed involving a preequilibrium between **8a** and its anion (the pK_a of **8a** can be estimated[26] to be about 8.5), rate-determining rearrangement of the anion via a transition state possibly similar to **12**, and a fast proton transfer to complete the reaction.

Table I. Pseudo-First-Order Rate Constants of the Rearrangement of 8a into 11a in 0.1 M Glycine Buffers at Ionic Strength 0.1 M and 33 °C

pH	k, s^{-1}	pH	k, s^{-1}
1.15	8.85×10^{-5}	3.05[a,b]	4.99×10^{-3}
1.65	2.35×10^{-4}	3.30	9.04×10^{-3}
2.10	6.16×10^{-4}	3.65	1.61×10^{-2}
2.75[a]	2.75×10^{-3}		

[a] Identical rate constants were obtained in 0.05 M glycine buffers (ionic strength 0.1 M). [b] $k = 5.72 \times 10^{-3}$ at ionic strength 0.3 M.



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At pH 0.5 the half-life of **8a** is thus around 10 h (cf. Table I), and no significant loss of material by rearrangement takes place during its preparation from **1f**. At pH 4 the half-life of **8a** would be on the order of 15 s, and so oxidation of **1f** at this pH was not investigated. From the crude reaction product obtained after oxidation at pH 0.5 (5 molar equiv of chlorite was necessary to consume all the substrate) the hydrate crystallized with some difficulty, and the practically attainable yield was at most 10%. However, the actual yield approached 30%, as shown by reduction of the crude, oily reaction product with zinc in acetic acid and acetic anhydride to give **9** along with the rearranged product **11c**. The cyclopentenones **11a** and **11c**, unlike **11b**, were unstable, and analytical samples of these compounds were not obtained; decarboxylation, likely accompanied by loss of chlorine, presumably accounts for their instability.

Although it is believed that chlorine dioxide is the species responsible for the formation of 2,4-hexadienedioates from monoethers of 1,2-diphenols on oxidation with chlorous acid,[13,16] we feel that speculations about the detailed mechanism of the ring cleavage would be premature. The reactions described in this work, as in the majority of studies reported in the literature, show poor material balance, the substrates being apparently extensively degraded.[27] The chlorous acid oxidation cannot at present be regarded as a general method for preparation of 2,4-hexadienedioates from aromatic precursors. Nevertheless,

(19) Jaroszewski, J. W.; Ettlinger, M. G. *J. Org. Chem.*, in press.
(20) For a review, see: McOmie, J. F. W.; Blatchly, J. M. *Org. React. (NY)* **1972**, *19*, 199. It should be noted that in Thiele–Winter acetoxylations acetoxy groups never enter positions next to a methoxy group.
(21) Graebe, C.; Hess, H. *Justus Liebigs Ann. Chem.* **1905**, *340*, 232.
(22) (a) The conversions of **5b** and **5d** to the corresponding triacetates parallel similar transformations described earlier[22b] in the bromomethoxy quinone series. (b) Blatchly, J. M.; Green, R. J. S.; McOmie, J. F. W.; Searle, J. B. *J. Chem. Soc. C* **1969**, 1353.
(23) Selman, S.; Easthan, J. F. *Q. Rev., Chem. Soc.* **1960**, *14*, 221.
(24) Zincke, T. *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 2493. Zincke, T.; Frölich, C. *Ibid.* **1887**, *20*, 1265, 2890. Zincke, T.; Gerland, C. *Ibid.* **1887**, *20*, 3216; **1888**, *21*, 2379. Zincke, T. *Ibid.* **1888**, *21*, 491. Zincke, T.; Küster, F. *Ibid.* **1888**, *21*, 2719; **1889**, *22*, 486. Zincke, T.; Arnst, T. *Justus Liebigs Ann. Chem.* **1892**, *267*, 319. Zincke, T.; Engelhardt, M. *Ibid.* **1894**, *283*, 341. Sucrow, W.; Wanzlick, H.-W. *Chem. Ber.* **1959**, *92*, 2516.
(25) Similar ring contractions occur during oxidation of phenols with alkaline hypochlorite, e.g.: Christie, R. M.; Rickards, R. W.; Schmalzl, K. J.; Taylor, D. *Aust. J. Chem.* **1977**, *30*, 2195.
(26) From the Taft equation given by: Hine, J.; Koser, G. F. *J. Org. Chem.* **1971**, *36*, 1348. The structure of **8a** was approximated by $CH_3C(OCCl_2(CH_3CO)C(OH)_2$, a value of 2.5 being adopted as the σ^* constant of CH_3COCCl_2.
(27) The complexity of the reaction between chlorine dioxide and a monoether of a 1,2-diphenol was well illustrated recently: Strumila, G. B.; Rapson, W. H. *Trans. Tech. Sect. (Can. Pulp Pap. Assoc.)* **1978**, *4*, TR34. However, very few of the large number of products observed in this study can be regarded as conclusively identified.

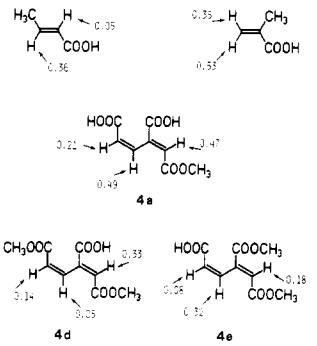

Figure 1. Upfield shifts in parts per million of olefinic protons in **4a,d,e** and model compounds caused by ionization of carboxy groups [$\delta(D_2O) - \delta(D_2O/NaHCO_3)$].

in a limited number of cases the reaction may have practical interest. Especially interesting are cases where the ring-cleavage products still contain an unoxidized aldehyde group, masked by formation of a cyclic hemiacetal, as in **3a–d**. Since the apparent spectrophotometric pK_a of **3a** is 5.6[28] and the pK_a of **2a** can hardly be more than 3.6,[29] the pH-independent equilibrium constant for cyclization of the latter is more than 10^2, which appears to afford sufficient kinetic protection against aldehyde oxidation at pH 4.[30] The cyclization is, however, not protective at pH 0.5, i.e., at a high ratio of chlorous acid to chlorite, where formation of **4a** from **3a** is quantitative.[9] On the other hand, oxidation of **1d** at pH 0.5 yielded more **3d** than **4b**. Since we find that the apparent spectrophotometric pK_a of **3d** is 4.0, the increase of acidity relative to **3a** being close to the expected[31] increase of acidity of **2b** relative to **2a**, the equilibrium between **2b** and **3d** is not significantly different from that between **2a** and **3a**. Thus, the electron-withdrawing effect of chlorine may be the primary factor responsible for suppression of the oxidation of the aldehyde group in **2b**.

Finally, we take the opportunity to comment on the previously unassigned structure of the monoacid dimethyl ester formed[9,11] on acid-catalyzed esterification of **4a** with methanol. We found that methylation of **4a** with 1 molar equiv of diazomethane yields mainly a diester different from the preceding. Ionization of the free carboxy groups of the diesters caused upfield shifts of the ^1H NMR signals of their olefinic protons, which on comparison with the corresponding shifts observed in model compounds [**4a**, (*E*)-2-butenoic acid, 2-methyl-2-propenoic acid] allowed unambigous assignment of structure **4d** to the diester obtained on esterification with methanol and structure **4e** to the product of diazomethane methylation (Figure 1). The same conclusion can be attained by comparing the ultraviolet absorption of the diesters in acid and base; ionization of the free carboxy group in **4d**, unlike that in **4e**, does not influence the spectrum significantly (see Experimental Section), showing that in **4d** the unesterified carboxy group is cross-conjugated to the 2,4-hexadienedioate chromophore. Thus monoesterification of **4a** with methanol appears to be sterically controlled, while diazomethane primarily attacks the more acidic carboxy group of **4a**.

Experimental Section

^1H NMR spectra were recorded at 60 MHz with Varian A60 or T60A spectrometers. IR and UV spectra were respectively obtained with Perkin-Elmer Model 457 and Unicam SP1800 spectrophotometers. Electron-ionization mass spectra were measured on an AEI MS902 spectrometer; field-desorption mass spectra were obtained with a Varian MAT CH5 instrument. Elemental analyses were performed in the microanalytical department of this Laboratory. Melting points were determined in capillaries and are corrected. Merck Kieselgel 60 (0.063–0.2 mm) was used for column chromatography. Sodium chlorite was obtained from Fluka and contained 79.5–81.5% of active oxidant (standardized iodometrically).

Methyl (*E*)-(2-Hydroxy-6-oxo-3,6-dihydro-2*H*-pyran-3-ylidene)acetate (3a).[9] A suspension of 30 g (0.197 mol) of **1a** in 1.5 L of citrate–phosphate buffer (pH 4, 0.4 M citric acid and 0.8 M Na_2HPO_4) was chilled to −5 °C, and a cold (0 °C) solution of 0.79 mol of $NaClO_2$ (89 g of 80% salt) in the least amount of water was added with stirring over a period of 20–30 min, keeping the temperature below 0 °C. The stirring was continued until a clear, bright yellow solution was obtained (ca. 20 min). The solution was degassed under suction or purged with nitrogen and extracted with five 400-mL portions of cold (0 °C) ether. The extracts were dried ($MgSO_4$) and evaporated in vacuo to a small volume without appreciable warming. The white crystals deposited were recrystallized from ether or benzene; yield 7–8 g (19–22%). The product (lit.[9] mp 104–105 °C) crystallized in one of two forms, mp 103–105 (usual) or 97–99 °C (unstable, giving the high-melting form on storage). The polymorphs differed in their IR absorption in the regions 3400–3200 and 1500–400 cm^{-1}, but both exhibited bands at 1720 (s), 1650 (w), and 1590 (w) cm^{-1}; the IR spectra in solution were identical. The ^1H NMR spectrum was as in the literature.[11]

Esters of (1*E*,3*Z*)-1,3-Butadiene-1,2,4-tricarboxylic Acid (4a,d,e). The mother liquid obtained after the extraction of **3a** in the foregoing preparation was acidified to pH 1 with H_2SO_4 and extracted several times with ether. From the extract 0.8 g (2%) of **4a** crystallized on concentration: mp 146 °C (lit.[9] mp 143–144 °C); IR (KBr) 3200–2500 (m), 1725 (s), 1710 (s), 1690 (s), 1650 (m), 1610 (m) cm^{-1}; UV λ_{max} 245 nm (ϵ 9800; in 0.01 M HCl), 255 (8200; at pH 7, phosphate buffer); ^1H NMR (D_2O) δ 3.82 ($COOCH_3$), 6.22 (H4), 6.80 (H1), 7.22 (H3) ($^3J_{3,4}$ = 12 Hz, $^4J_{1,3}$ = 2.2 Hz, $^5J_{1,4}$ = 1 Hz);[11] in D_2O saturated with $NaHCO_3$ the respective δ values were 3.73, 6.01, 6.33, and 6.73 ($^3J_{3,4}$ = 12.1 Hz, $^4J_{1,3}$ = 1.8 Hz, $^5J_{1,4}$ = 0.8 Hz). The same product (melting and mixture melting point, IR, ^1H NMR) was obtained in 20–25% yield by chlorous acid oxidation of **1a** at pH 0.5 (H_2SO_4).[9]

The dimethyl ester **4d** was obtained from **4a** by esterification with methanol:[9,11] mp 124–126 °C (lit.[11] mp 124–125 °C); IR (KBr) 3200–2500 (w), 1725 (s), 1715 (s), 1700 (s), 1650 (w), 1610 (m) cm^{-1}; UV λ_{max} 245 nm (ϵ 9800; in 0.01 M HCl), 240 (sh, 10 200; at pH 7, phosphate buffer); ^1H NMR ($CDCl_3$) δ 3.70 and 3.78 ($COOCH_3$), 6.15 (H4), 6.83 (H1), 7.19 (H3), 10.5 (COOH) ($^3J_{3,4}$ = 12 Hz, $^4J_{1,3}$ 2.0 Hz, $^5J_{1,4}$ = 1 Hz);[11] in D_2O the respective δ values were 3.72, 3.77, 6.20, 6.75, and 7.18; in D_2O saturated with $NaHCO_3$ they were δ 3.67, 3.73, 6.06, 6.42, and 7.13.

The dimethyl ester **4e** was obtained by treatment of **4a** in ether–methanol (1:1) with 1 mol of diazomethane and column chromatography [benzene–ethyl acetate (4:1) containing 2% of acetic acid] of the product; **4e** (yield 60%) was eluted after small amounts of the corresponding trimethyl ester:[11] mp 60–61 °C (from ether–pentane); IR (KBr) 3300–2500 (m), 1715 (s), 1700 (s), 1660 (m), 1610 (s) cm^{-1}; UV λ_{max} 244 nm (ϵ 9500; in 0.01 M HCl), 255 (9000; at pH 7, phosphate buffer); ^1H NMR ($CDCl_3$) δ 3.78 (2 $COOCH_3$), 6.14 (H4), 6.77 (H1), 6.97 (H3), 8.8 (COOH) ($^3J_{3,4}$ = 12 Hz, $^4J_{1,3}$ = 2.2 Hz, $^5J_{1,4}$ = 1 Hz]; in D_2O the respective δ values were 3.79, 6.22, 6.75, and 7.20; in D_2O saturated with $NaHCO_3$ they were δ 3.77, 6.14, 6.57, and 6.88.

Anal. Calcd for $C_9H_{10}O_6$: C, 50.47; H, 4.71. Found: C, 50.35; H, 4.87.

(28) Ettlinger, M. G.; Jaroszewski, J. W. *Tetrahedron Lett.* **1980**, 21, 3503.

(29) Cf. for example: Barlin, G. B.; Perrin, D. D. *Q. Rev., Chem. Soc.* **1966**, *20*, 75. In the absence of a closer model, the acid-strengthening effects of *m*-formyl and *p*-methoxycarbonyl groups in benzoic acid (respectively 0.36 and 0.39 logarithm units) may be subtracted from the pK_a of propenoic acid (4.26).

(30) (a) Weakly acidic chlorite solutions readily oxidize unprotected aldehyde groups; apart from the formation of **6** from **1e**, a number of examples have been reported.[17c,30b] (b) Lindgren, B. O.; Nilsson, T. *Acta Chem. Scand.* **1973**, *27*, 888. Bal, B. S.; Childers, W. E., Jr.; Pinnick, H. W. *Tetrahedron* **1981**, *37*, 2091.

(31) Cf. the acid-strengthening effect of α-chlorine in model compounds, e.g.: Charton, M. *J. Org. Chem.* **1965**, *30*, 557.

Ethyl (*E*)-(2-Hydroxy-6-oxo-3,6-dihydro-2*H*-pyran-3-yl-idene)acetate (3b). Oxidation of **1b** was carried out at pH 4 as described for **1a**; 15 g of **1b** yielded 3 g (17%) of **3b**: mp 88–89 °C (from ether–petroleum ether); IR (KBr) 3270 (br, s), 1720 (s), 1650 (w), 1590 (w) cm^{-1}; UV (0.01 M HCl) λ_{max} 265 nm (ϵ 19 000); ^1H NMR ($CDCl_3$) δ 1.33 and 4.27 (CH_2CH_3; ^3J = 7.5 Hz), 5.9 (OH), 6.10 (H2 or Hα), 6.20 (H5), 6.28 (Hα or H2), 8.22 (H4) ($^3J_{4,5}$ = 10 Hz; the signals of Hα, H2, H4, and H5 show fine structure owing to long-range coupling).

Anal. Calcd for $C_9H_{10}O_5$: C, 54.55; H, 5.09. Found: C, 54.60; H, 5.18.

Methyl (*E*)-(2-Hydroxy-5-methyl-6-oxo-3,6-dihydro-2*H*-pyran-3-ylidene)acetate (3c). Oxidation of **1c**[32] was carried out at pH 4 as described for **1a**; 1 g of the substrate yielded 70 mg (6%) of **3c**: mp 117–119 °C (from ether–petroleum ether); IR (KBr) 3320 (br, s), 1725 (s), 1700 (s), 1650 (m), 1610 (w) cm^{-1}; UV (0.01 M HCl) λ_{max} 276 nm (ϵ 19 000); ^1H NMR ($CDCl_3$) δ 2.12 (CH_3), 3.81 (OCH_3), 5.2 (OH), 6.07 and 6.14 (H2 and Hα), 8.08 (H4) (the signals of Hα, H2, H4, and CH_3 show fine structure owing to long-range coupling); exact mol wt calcd for $C_9H_{10}O_5$ 198.0528, found 198.0585.

Methyl (*E*)-(5-Chloro-2-hydroxy-6-oxo-3,6-dihydro-2*H*-pyran-3-ylidene)acetate (3d) and Trimethyl (1*E*,3*E*)-4-Chloro-1,3-butadiene-1,2,4-tricarboxylate (4c). To 15 g (0.08 mol) of **1d**[33] suspended in 500 mL of H_2SO_4 (pH 0.5) was added a solution of 0.32 mol of $NaClO_2$ (36 g of 80% salt) in the least amount of water at room temperature. After being stirred for 30 min, the solution was filtered to give 4 g of **1d** (27% recovery) and extracted with five 150-mL portions of ether. The extracts were dried ($MgSO_4$) and evaporated; the ^1H NMR spectrum ($CDCl_3$) of the crude product indicated the presence of **3d** and **4b** [δ 3.78 ($COOCH_3$), 6.81 (H1), 7.52 (H3); $^4J_{1,3}$ = 2.2 Hz] in a 3:1 ratio. Column chromatography (benzene–ethyl acetate, 4:1) yielded three fractions. The first fraction contained 50 mg of a yellow material, which after recrystallization from ethanol melted at 164–166 °C [IR (KBr) 1690 (s), 1650 (s), 1620 (s), 1570 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.92 (s, 3 H), 6.13 (s, 1 H)], thus evidently being **5a** (lit.[34] mp 160 °C dec).[18]

The second fraction contained 0.4 g (2%) of **3d**: mp 129–130 °C (from ether–pentane); IR (KBr) 3350 (br, s), 1725 (s), 1710 (s), 1640 (w), 1575 (w) cm^{-1}; UV λ_{max} 283 nm (ϵ 19 300; in 0.01 M HCl), 276 (7500; at pH 8, phosphate buffer); spectrophotometric pK_a = 4.0; ^1H NMR [$(CD_3)_2CO$] δ 3.82 ($COOCH_3$), 6.46 (Hα and H2), 7.5 (OH), 8.41 (H4) (the signals of Hα, H2, and H4 show fine structure owing to long-range coupling); mass spectrum, *m/e* (relative intensity %) 218 (38, M); 183 (100, M – Cl) (m* for the Cl· loss observed).[35]

Anal. Calcd for $C_8H_7O_5Cl$: C, 43.96; H, 3.23; Cl, 16.22. Found: C, 44.15; H, 3.36; Cl, 16.35.

The third fraction, containing tarry material, was treated with excess ethereal diazomethane to give, after column chromatography in chloroform–benzene (2:1), 0.1 g (0.5%; some may have reacted further with the diazomethane) of oily **4c**: IR (neat) 1725 (s), 1640 (m), 1595 (m) cm^{-1}; UV CH_3OH) shoulder at 250 nm; ^1H NMR ($CDCl_3$) δ 3.78 (3 $COOCH_3$), 6.77 (H1), 7.48 (H3) ($^4J_{1,3}$ = 2.2 Hz); mass spectrum, *m/e* (relative intensity %) 262 (10, M), 227 (100, M – Cl) (m* for the Cl· loss observed);[35] exact mol wt calcd for $C_{10}H_{11}O_6{}^{35}Cl$ 262.0244, found 262.0234.

(*Z*)-4-(Methoxycarbonyl)-1,3-butadiene-1,1-dicarboxylic Acid (6). Oxidation of 30 g of **1e** in H_2SO_4 (pH 0.5) was carried out similarly to the oxidation of **1a** at pH 4 to give **6**: 2.8 g (7%); mp 141–142 °C dec (from ether–petroleum ether); IR (KBr) 3300–2500 (s), 1740–1680 (s), 1595 (m) cm^{-1}; UV λ_{max} 269 nm (ϵ 20 000; in 0.1 M HCl), 280 (17 500; at pH 7, phosphate buffer); ^1H NMR [$(CD_3)_2CO$] δ 3.78 ($COOCH_3$), 6.26 (H4), 7.32 (H3), 8.68 (H2), 11.4 (2 COOH) ($^3J_{2,3}$ = 11.5 Hz, $^3J_{3,4}$ = 11.5 Hz, $^4J_{2,4}$ = 1 Hz).

Anal. Calcd for $C_8H_8O_6$: C, 48.01; H, 4.03. Found: C, 48.09; H, 4.28.

Oxidation of **1e** at pH 4, similarly to **1a**, gave **5b** (3% yield), which was extracted with ether at pH 4 [mp 155–157 °C; IR (KBr) 1700 (s), 1640 (s), 1625 (s), 1585 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.88 (OCH_3), 5.98 (H3), 6.93 (H5) ($^4J_{3,5}$ = 2 Hz)] and was identical in all respects (melting and mixture melting point, IR, ^1H NMR) with an authentic[36] sample, and **6** (yield 7%), which was extracted with ether after acidification to pH 0.5 with H_2SO_4.

Catalytic hydrogenation of **6** on $Pt/BaSO_4$ in ether at ambient temperature and pressure gave **7** quantitatively: mp 83–84 °C (from ether–petroleum ether); IR (KBr) 3200–2500 (m), 1735 (s), 1715 (s) cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 1.65 (m, CH_2CH_2), 2.32 (br t, CH_2CO), 3.20 (t, ^3J = 6.5 Hz, CH), 3.59 (s, $COOCH_3$).[37] Heating of this compound for a few minutes at 160–165 °C caused quantitative decarboxylation to oily monomethyl hexanedioate, identical (IR, ^1H NMR) with an authentic sample.

Anal. Calcd for $C_8H_{12}O_6$: C, 47.06; H, 5.92. Found: C, 47.20; H, 6.07.

Methoxy-1,4-benzoquinone (5c). To 5 g (0.04 mol) of 2-methoxyphenol in 150 mL of H_2SO_4 (pH 0.5) was added a solution of 0.16 mol of $NaClO_2$ (18 g of 80% salt) in the least amount of water at 0 °C. The mixture was stirred for 15 min and filtered to give 2 g of **5c**. Additional material (0.5 g) was obtained by extraction of the filtrate with three 100-mL portions of ether; total yield 45%. The product (mp 144–145 °C, after recrystallization from ether) was identical in all respects (melting and mixture melting point, IR, ^1H NMR) with an authentic sample obtained[38] from **1a**.

5,5-Dichloro-6,6-dihydroxy-2-methoxy-2-cyclohexene-1,4-dione (8a). Oxidation of **1f** was carried out as described for the oxidation of **1a** at pH 4 but in H_2SO_4 (pH 0.5) and with 5 molar equiv of oxidant. Extraction with ether and crystallization of the crude reaction product from ether–petroleum ether gave pure **8a**; 10 g of **1f** yielded about 1.5 g (9.5%) of the material: mp 149 °C dec; IR (KBr) 3450 (m), 3400 (m), 1730 (s), 1710 (s), 1610 (s) cm^{-1}; UV λ_{max} 214 nm (ϵ 5000) and 282 (10 100) in acetonitrile, 281 nm in 0.01 M HCl; ^1H NMR [$(CD_3)_2CO$] δ 3.93 (OCH_3), 6.22 (olefinic H), 6.90 (sharp, 2 OH); mass spectrum (field desorption), *m/e* 240/242 (M); 222/224 (M – H_2O) (no molecular ion in electron-impact spectrum).

Anal. Calcd for $C_7H_6O_5Cl_2$: C, 34.88; H, 2.51; Cl, 29.42. Found: C, 34.70; H, 2.40; Cl, 29.40.

Reduction of the crude reaction product from 1 g of **1f** with Zn dust in ether–acetic anhydride–acetic acid (1:1:1) overnight and column chromatography (benzene–ethyl acetate, 4:1) gave 0.5 g (24%) of **9** (mp 109–110 °C; see later) and 0.1 g (5%) of **11c**, obtained as a colorless gum: ^1H NMR ($CDCl_3$) δ 2.13 ($COCH_3$), 4.02 (OCH_3), 5.82 (olefinic H); UV (CH_3OH) λ_{max} 245 nm. The substance decomposed on being allowed to stand at room temperature for a few days.

5,5-Dichloro-2,6-dimethoxy-6-hydroxy-2-cyclohexene-1,4-dione (8b). The hemiacetal was obtained in quantitative yield by refluxing **8a** (1 g) in 3% methanolic HCl (100 mL) for 3 h. Evaporation left an oil, which solidified on standing. The product was recrystallized from dry ether (freshly passed through anhydrous alumina); mp 128–131 °C. Sublimation [60 °C (0.01 mmHg)] gave **8b** as long thin needles with the same melting point: IR (KBr) 3460 (s), 1735 (s), 1700 (s), 1605 (s) cm^{-1}; UV (ether) λ_{max} 281 nm; ^1H NMR ($CDCl_3$) δ 3.31 (OCH_3), 3.92 (olefinic OCH_3), 4.90 (OH), 6.12 (olefinic H). In wet solvents **8b** was rapidly reconverted to **8a**.

Anal. Calcd for $C_8H_8O_5Cl_2$: C, 37.67; H, 3.16. Found: C, 37.85; H, 3.08.

5,5-Dichloro-1-hydroxy-2-methoxy-4-oxo-2-cyclopentene-carboxylic Acid (11a). The hydrate **8a** (0.15 g) in 5 mL of water was treated with saturated aqueous bicarbonate to obtain neutral

(32) Obtained according to: Freudenberg, K.; Jovanovič, V.; Topfmeier, F. *Chem. Ber.* **1961**, *94*, 3227.

(33) Obtained according to: Raiford, L. C.; Lichty, J. G. *J. Am. Chem. Soc.* **1930**, *52*, 4576.

(34) Castelfranchi, G.; Oliverio, A.; Scrocco, M. *Gazz. Chim. Ital.* **1956**, *86*, 371.

(35) Cf.: Mandelbaum, A.; Weinstein, S.; Gil-Av, E.; Leftin, J. H. *Org. Mass Spectrom.* **1975**, *10*, 842.

(36) The quinones **5b** and **5d** were obtained via Dakin oxidation of 3- and 2-chloro-4-hydroxy-5-methoxybenzaldehyde,[33] respectively: Asp, L.; Lindberg, B. *Acta Chem. Scand.* **1950**, *4*, 60. Cf.: Joffe, J. S.; Sukhina, A. F. *Zh. Obshch. Khim.* **1953**, *23*, 295; *J. Gen. Chem. USSR (Engl. Transl.)* **1953**, *23*, 307.

(37) Cf. ^1H NMR spectrum of the corresponding trimethyl ester: Brettle, R.; Cummings, D. P. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2177.

(38) Erdtman, H. *Sven. Kem. Tidskr.* **1932**, *44*, 135. Erdtman, H. G. H. *Proc. R. Soc. London, Ser. A* **1933**, *143*, 177.

solution. Acidification (0.1 M HCl) and extraction with ether gave about 0.14 g (93%) of **11a** as a colorless, partly crystalline material:[39] UV (0.01 M HCl) λ_{max} 255 nm; ^{1}H NMR [$(CD_3)_2CO$] δ 4.04 (OCH_3), 5.82 (olefinic H), 8.0 (br, OH and COOH). Attempts to recrystallize the substance from ether resulted in gradual decomposition, accompanied with generation of chloride ions.

Methyl 5,5-Dichloro-1-hydroxy-2-methoxy-4-oxo-2-cyclopentenecarboxylate (11b). A solution of 70 mg of **8b** in methanol (5 mL) was treated with a trace of triethylamine. Evaporation and recrystallization from ether–petroleum ether gave 60 mg (85%) of **11b**:[39] mp 130–131 °C; IR (KBr) 3400 (br, s), 1760 (s), 1725 (s), 1610 (s) cm^{-1}; UV (CH_3OH) λ_{max} 246 nm (ϵ 13 800); ^{1}H NMR ($CDCl_3$) δ 3.85 ($COOCH_3$), 3.96 (olefinic OCH_3), 4.5 (OH), 5.58 (olefinic H).

Anal. Calcd for $C_8H_8O_5Cl_2$: C, 37.67; H, 3.16; Cl, 27.80. Found: C, 37.67; H, 3.43; Cl, 27.70.

2-Chloro-5-methoxy-1,3,4-triacetoxybenzene (9). A solution of **8a** (0.4 g) in 30 mL of ether–acetic anhydride–acetic acid (1:1:1) was stirred overnight with 5 g of Zn dust. After filtration and evaporation, the residue was chromatographed in benzene–ethyl acetate (4:1) to give 0.4 g (76%) of **9**. From ether–petroleum ether the product could be obtained in two crystalline modifications: slow crystallization gave needles (mp 111 °C), whereas rapid crystallization yielded prisms (mp 114.5 °C). The two forms differed in their IR absorption in KBr in the 1500–400-cm^{-1} region but gave identical IR spectra in $CHCl_3$ and could be repeatedly reconverted into one another by slow or rapid recrystallization: IR (KBr) 1780 (s), 1615 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.23 and 2.28 (respectively 1 and 2 $COCH_3$), 3.75 (OCH_3), 6.73 (aromatic H).

Anal. Calcd for $C_{13}H_{13}O_7Cl$: C, 49.30; H, 4.14; Cl, 11.19. Found: C, 49.35; H, 4.14; Cl, 11.28.

The same product (melting and mixture melting point, IR, ^{1}H NMR) was obtained by Thiele–Winter acetoxylation of **5d**. Thus a solution of the quinone[36] (0.1 g) in 4 mL of freshly redistilled acetic anhydride was treated with 4 drops of $HClO_4$. After 10 days at room temperature the solution was stirred with water and ice until the anhydride was hydrolyzed and was extracted with ether to give 0.18 g (98%) of **9**. A slightly lower yield of **9** was obtained from **5d** with BF_3 etherate as a catalyst, but no reaction was observed with H_2SO_4 (over 90% recovery of **5d**).

3-Chloro-5-methoxy-1,2,4-triacetoxybenzene (10). A solution of **5b**[36] (0.45 g) in 10 mL of freshly redistilled acetic anhydride was treated with 0.5 mL of BF_3 etherate or H_2SO_4 or 0.2 mL of $HClO_4$ and left for 3 days at room temperature. The solutions were poured into water and ice and stirred until the anhydride was hydrolyzed, and the precipitates were recrystallized from ether–petroleum ether. Each experiment gave ca. 0.35 g (42%) of the same material: mp 136–138 °C; IR (KBr) 1780 (s), 1615 (m), 1590 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.27, 2.30 and 2.33 ($COCH_3$ groups), 3.80 (OCH_3), 6.77 (aromatic H).

Anal. Calcd for $C_{13}H_{13}O_7Cl$: C, 49.30; H, 4.14; Cl, 11.19. Found: C, 49.55; H, 4.04; Cl, 11.12.

2-Chloro-3-hydroxy-5-methoxy-1,4-benzoquinone (5e). The triacetate **9** (2 g) was refluxed in 100 mL of 0.5% methanolic H_2SO_4 during 1 h under nitrogen. The solution was diluted with an equal volume of water, the methanol evaporated in vacuo, and the residue extracted with six 50-mL portions of ether. The extracts were evaporated, and the residue was dissolved in water, acidified with diluted HCl, and treated with an excess of aqueous $FeCl_3$. The red precipitate was filtered off, washed with water, and recrystallized from ether to give 0.65 g (55%) of the product: mp 226–228 °C dec (sealed tube); IR (KBr) 3200 (br, s), 1700 (s), 1670 (m), 1640 (s), 1605 (s) cm^{-1}; ^{1}H NMR [$(CD_3)_2SO$] δ 3.79 (OCH_3), 6.08 (olefinic H), 10.5 (br, OH).

Anal. Calcd for $C_7H_5O_4Cl$: C, 44.59; H, 2.67; Cl, 18.80. Found: C, 44.39; H, 2.46; Cl, 18.82.

The quinone was methylated with diazomethane[40] to give **5f**, purified by column chromatography (benzene–ethyl acetate, 4:1), and recrystallized from ethanol: mp 147–148 °C (lit.[21] mp 148 °C); IR (KBr) 3070 (m), 1690 (s), 1650 (s), 1640 (s), 1590 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.87 and 4.17 (OCH_3), 5.98 (olefinic H). The material was indistinguishable (mixture melting point, IR, ^{1}H NMR) from an authentic[41] sample.

Kinetic Measurements. Glycine–NaCl solutions (0.1 M in each) were titrated with 0.1 M HCl to obtain the required pH meter readings. Buffers with other concentrations or ionic strengths were prepared similarly. Aliquots of the buffers (ca. 3 mL; preheated to 33 °C) were mixed in a UV cell (1 cm; thermostated at 33 °C) with appropriate samples of **8a** in acetonitrile (ca. 10 μL), and the absorbance at 255 nm was recorded until a constant final value was obtained. Rate constants were derived from the resulting kinetic plots by the least-squares method. Each constant was determined at least twice; in the pH region 1.65–3.30 results varied less than 1% from the mean values reported in Table I, whereas at the extreme pH values (1.15 and 3.65) deviations up to 6% from the mean values of three runs (Table I) were observed. The stability of the product was tested at pH 1.15; the loss of absorption of **11a** at 255 nm during 5 h was about 2%.

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Registry No. **1a**, 121-33-5; **1b**, 121-32-4; **1c**, 32263-14-2; **1d**, 19463-48-0; **1e**, 148-53-8; **1f**, 621-59-0; **3a**, 81158-22-7; **3b**, 81158-23-8; **3c**, 81158-24-9; **3d**, 81158-25-0; **4a**, 81158-26-1; **4b**, 81158-27-2; **4c**, 81158-28-3; **4d**, 81158-29-4; **4e**, 81158-30-7; **5a**, 81158-31-8; **5b**, 54490-80-1; **5c**, 2880-58-2; **5d**, 24605-23-0; **5e**, 81158-32-9; **5f**, 24605-25-2; **6**, 81158-33-0; **7**, 81158-34-1; **8a**, 81158-35-2; **8b**, 81158-36-3; **9**, 81158-37-4; **10**, 81158-38-5; **11a**, 81158-39-6; **11b**, 81158-40-9; **11c**, 81158-41-0; monomethyl 1,6-hexanedioate, 627-91-8; 2-methoxyphenol, 90-05-1; $NaClO_2$, 7758-19-2.

(39) The rearrangement was apparently instant and quantitative when the reaction was carried out in deuterated solvents and observed directly by ^{1}H NMR.

(40) Cf.: Lindberg, B. *Acta Chem. Scand.* **1952**, *6*, 1084. Reference 22b, Appendix.

(41) I thank Professor Bengt Lindberg, Arrhenius Laboratory, University of Stockholm, for a sample of authentic **5f**.