Chlorous Acid Oxidation of Trifluoromethylphenols: Cyclopentenolones by Benzilic Acid Ring Contraction

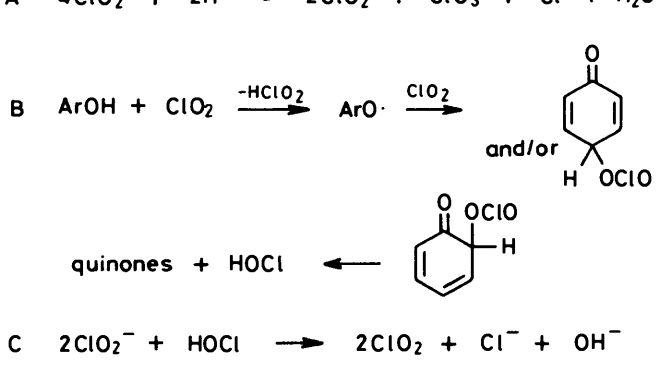
Jean-Claude Blazejewski, Régine Dorme, and Claude Wakselman*
CNRS-CERCOA, 2 rue Henri Dunant, 94320 Thiais, France

The formation of 2-chloro-2-trifluoromethylcyclopentane-1,3-dione (**1**) in the chlorous acid oxidation of 2- and 3-trifluoromethylphenol is shown to proceed *via* decarboxylation of 5-chloro-1-hydroxy-4-oxo-5-trifluoromethylcyclopent-2-enecarboxylic acid (**4**), an isolable compound.

We recently reported the synthesis of 2-chloro-2-trifluoromethylcyclopentane-1,3-dione (**1**) by chlorous acid oxidation of 3-trifluoromethylphenol[1] (**11**). This chlorinated ketone was easily reduced to 2-trifluromethylcyclopentane-1,3-dione (**2**), a very useful synthon for the preparation of steroids angularly substituted by a trifluoromethyl group.[2]

In view of the biological significance of fluorinated steroids, we planned to study this reaction more closely in order to shed some light on the mechanism of formation of the diketone (**1**) and eventually increase its yield.

Chlorite is unable to oxidize phenols directly, its transformation into chlorine dioxide first being necessary.[3] Aqueous solutions of chlorous acid (acidified chlorite), which decompose spontaneously at low pH leading to chlorine dioxide as the main product,[4] can fulfil this role (Scheme 1,A).



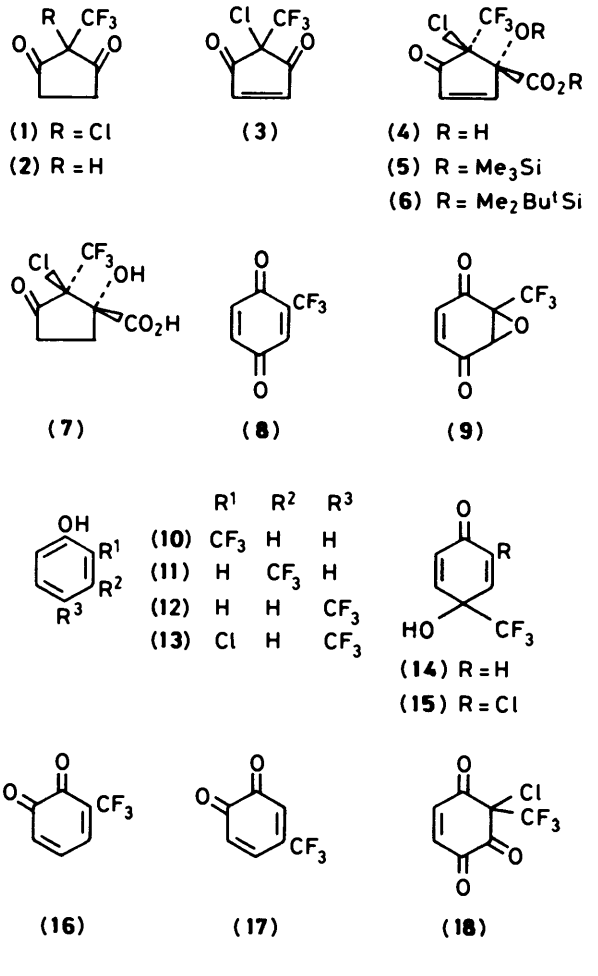
Scheme 1.

The first event in the reaction between a phenolic compound and chlorine dioxide is thought to be a one-electron transfer from the phenol to chlorine dioxide leading to a phenoxyl radical and chlorous acid.[3,5] This radical can react further, adding a further molecule of chlorine dioxide on the *para* or one of the two *ortho* positions, to give respectively the chlorite esters of a *p*-quinol or an *o*-quinol. Loss of hypochlorous acid from these esters can lead to *p*- or *o*-quinones respectively (Scheme 1,B).

Since, besides ketone (**1**), we also observed the formation of 2-trifluoromethyl-*p*-benzoquinone (**8**) as a major product during the oxidation of phenol (**11**) by chlorous acid,[1] we speculate that (**1**) could be formed by a mechanism involving a quinonoid intermediate.

Each of the three isomeric quinones (**8**), (**16**), and (**17**) which could be formed from phenol (**11**) should, in principle, also be obtained during the oxidation of the two other isomers of trifluoromethyl phenol [*i.e.* quinones (**8**) and (**16**) from phenol (**10**) and quinone (**17**) from phenol (**12**)].

The study of the behaviour of 2- and 4-trifluoromethylphenol (**10**) and (**12**) toward this oxidizing agent was thus an obvious choice for a possible discrimination between the alternative pathways; *i.e.*, does ketone (**1**) arise *via* the intermediacy of quinone (**8**), (**16**), or (**17**)?

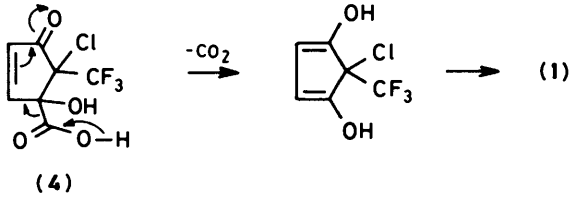


Results and Discussion

We had already noticed in our previous work[1] that after the oxidation of phenol (**11**), a refluxing period of the crude extract in acetonitrile was necessary to obtain ketone (**1**) and we thought that an intermediate was involved. We have now been able to isolate the unsaturated carboxylic acid (**4**), the precursor of (**1**), by crystallisation either by oxidation of phenol (**11**) or,

more satisfactorily, by oxidation of phenol (**10**). Upon simple melting or refluxing in acetonitrile this acid is quantitatively decarboxylated to ketone (**1**).

The structure of acid (**4**) was assigned on the basis of its spectroscopic properties and those of its silyl derivatives (**5**) and (**6**), prepared quantitatively by the action of the appropriate *N*-methyl-*N*-(trialkylsilyl)trifluoroacetamide. Thus the proton n.m.r. spectrum (60 MHz, CD_3CN) of acid (**4**) shows an AB quartet (J 6.1 Hz) centred at δ_H 7.2, and two exchangeable protons at δ_H 5.9. The trifluoromethyl group appears as a singlet (δ_F −68.2) in the fluorine n.m.r. spectrum pointing to a lack of coupled protons in close proximity. The thermal instability of the acid (**4**) precludes the recording of its ^{13}C n.m.r. spectrum. However, the spectra of its closely related silyl derivatives (**5**) and (**6**) proved most informative. Thus, as well as the signals given by the silyl groups, both compounds show two peaks at δ_C 190.8 (J_{CH} 4.2 and 9.8 Hz) and δ_C 176.1 (no coupling), attributed to the carbonyl carbon of an α,β-unsaturated ketone, shielded by the vicinity of chlorine and fluorine atoms,[6] and to the carbonyl atom of an isolated carboxyl group respectively. The unsaturated nature of the ketonic system was further confirmed by the presence of two ethylenic carbons at δ_C 133.4 (J^1_{CH} 180 Hz) and δ_C 160.3 (J^1_{CH} 176.1 Hz). The three remaining carbons were assigned to the trifluoromethyl group (δ_C 121.8, J_{CF} 284.4 Hz), the chlorinated carbon atom (δ_C 72.0, J_{CF} 27.6 Hz), and the tertiary carbon bearing the hydroxy group (δ_C 88.0, J_{CH} 3.3 and 10.2 Hz). The ^{13}C n.m.r. spectrum is thus fully consistent with the assigned structure (**4**) and reminiscent of those of halogenated cyclopentanoid congeners.[7,8] The transformation of acid (**4**) to ketone (**1**) can be considered to occur *via* the enol form of (**1**) (Scheme 2).*



Scheme 2.

Furthermore the double bond in acid (**4**) could easily be reduced by triethylsilane in trifluoroacetic acid[9] (82% yield) leading to the saturated analogue (**7**) which proved to be thermally stable and which had spectral characteristics fully consistent with its proposed structure (see Experimental section).

The acid (**4**) is obtained as a single diastereoisomer. We tentatively assigned this to the relative configuration 1*R**, 5*R** on the grounds of steric repulsion and maximization of intramolecular hydrogen bonds. The formation of a unique isomer during the ring contraction of an halogenated phenol is not without precedent; the formation of the Hantzsch acid is a well known example[7] of such a stereoselective reaction.

As a rule, in the oxidation of phenols with chlorous acid,[10] numerous by-products are formed and this was the case during oxidation of the phenols (**10**)—(**12**). Fortunately, in our case, these were usually present in minute amounts, and the material balance remained quite good. We were able to isolate the products by chromatography and identify some of these fluorinated compounds. The Table gives the percentage of the various products as determined by examination of the fluorine n.m.r. spectra of the crude ethereal extracts from typical experiments.

* We thank a referee for the suggestion of an intramolecular retro-ene reaction as an alternative mechanism.

Table. Oxidation reactions with chlorous acid

Substrate	Scale (g)	Temp. (°C)	Products (%) (1)	(3)	(4)	(8)	(9)	(19)	Unchanged
(**10**)	1	5—12	3	3	35	2	4	8	38[a]
(**10**)	5	5—15	2	9	60	2	4	5	6
(**11**)	1	5—7		8	13		4	6	66
(**11**)	5	5—20	2	6	36	20	4	7	5
(**11**)	13	5—35	1	15	20	40	5	6	2
(**12**)	1	5—10						14	61[b]
(**12**)	5	5—7						5	80[c]
(**8**)	1	5—8	8	24	33		6	7	
(**4**)	1	5—6	12	3	30			35	*d*

[a] For all entries, unidentified materials complements to 100%. [b] Also formed (**13**) (7%), (**14**) (9%), and (**15**) (2%). [c] Also formed (**13**) (3%), (**14**) (5%), and (**15**) (1%). [d] Starting material (**4**).

Thus, in the oxidation of phenols (**10**) and (**11**), together with acid (**4**) and quinone (**8**), we also observed the formation of the cyclopentenedione (**3**), which may arise from (**4**) by loss of formic acid, as well as the formation of the epoxyquinone (**9**) derived from (**8**), in varying amounts. As already noted, compound (**1**) is present in only small amounts in the crude extracts.

The phenol (**12**), which shows lower reactivity, also behaved quite differently to (**10**) or (**11**); the formation of (**4**) and (**8**) or products (**3**) and (**9**) derived therefrom was not observed, instead the known chlorophenol (**13**) and the corresponding *p*-quinols (**14**) and (**15**) resulting from the attack at the carbon atom bearing the trifluoromethyl group were isolated.

The chlorinated acid (**19**), the product of a more extensive degradation of the aromatic nucleus, was present in all the reactions.

As seen in the Table, the oxidation reactions are scale dependent. On a low scale (*e.g.* 1 g) most of the starting material remained unconsumed and only a small temperature rise, if any, was observed. Scaling up the reaction not only increased the consumption of starting phenol and gave a higher temperature rise, but it also altered the relative proportions of the products. Thus, a higher yield of quinone (**8**) was obtained on the 13 g scale than on the 5 g scale experiment with phenol (**11**).

These observations are in agreement with the character of a chain reaction usually observed in the oxidation of phenols with chlorite.[3,5,11] These chain reactions are initiated by the hypochlorous acid released during the formation of quinones (Scheme 1,B) which could react further with chlorite giving more chlorine dioxide[4] (Scheme 1,C).

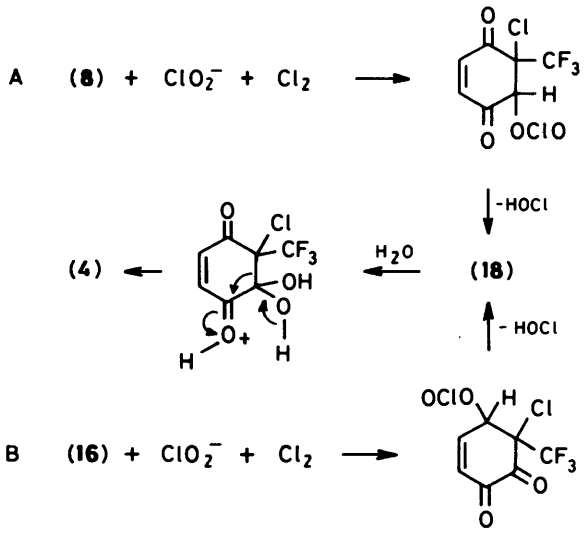
On these grounds, one tentatively proposes that on a small scale only short-chain reactions occur and that the formation of chlorine dioxide proceeds mainly by Scheme 1,A leaving most of the starting material unchanged. Moreover, the concentration of the nucleophilic chlorite anion[12] remains high in the medium, leaving room for side reactions with the products formed. On a larger scale, however, if the reaction proceeds essentially by the chain mechanism, most of the chlorite is quickly consumed and one can observe the primary products of the reaction with chlorine dioxide.

Since oxidation of phenol (**12**) did not lead to the formation of acid (**4**), the quinone (**17**) could be safely excluded from the reaction path to this compound. This left the alternative intermediates, the *p*-quinone (**8**) or the *o*-quinone (**16**), which could both be obtained from phenols(**10**) or (**11**).

Indeed, as seen in the Table, the reaction of the quinone (**8**) with chlorite, under the same conditions as used for the oxidation of phenols, gave the acid (**4**) efficiently. Further

reaction of (**4**) with chlorite produced mainly the acid (**19**) presumably *via* the dienones (**1**) or (**3**).

We thus propose (Scheme 3,A) that nucleophilic attack of the chlorite anion on the activated double bond of quinone (**8**) followed by electrophilic capture of the incipient carbanion with chlorine gives an intermediate chlorite ester which, by loss of hypochlorous acid, leads to the trione (**18**). Ring-contraction of this quinone (**18**) by a benzilic acid type rearrangement should thus give the acid (**4**). Such ring-contraction of halogenated quinones has already been noticed in the chlorous acid oxidation of isovanillin[10] and has been used in a synthesis of cryptosporiopsin.[13]



Scheme 3.

The quinone (**16**) could not be definitively excluded from the pathway to acid (**4**) since the same sequence of reactions on this quinone would lead to the same intermediate trione (**18**) (Scheme 3,B). Unfortunately this quinone was not available to test this hypothesis and attempted preparations of (**16**) *via* oxidation of phenol (**10**) with benzeneseleninic anhydride[14] or *via* oxidation of 3-trifluoromethyl catechol with silver carbonate on Celite[15] have so far been unsuccessful.

In conclusion, we have shown in this work that the formation of ketone (**1**) proceeds *via* decarboxylation of acid (**4**) and that the important synthon (**1**) is now available in *ca.* 50% yield by the chlorous acid oxidation of phenol (**10**) on a 5 g scale. Furthermore, the highly functionalised acid (**4**) may prove to be a valuable intermediate for the synthesis of other five-membered ring molecules containing the trifluoromethyl group.

Experimental

M.p.s were determined on a Mettler FP-61 apparatus. I.r. spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. ^{1}H and ^{19}F N.m.r. spectra were taken on Bruker WH-90 or Varian EM-360 L spectrometers using tetramethylsilane (TMS) and $CFCl_3$ respectively as internal standards. ^{13}C N.m.r. spectra were recorded on a Varian CFT-20 instrument with $SiMe_4$ as internal reference. The spectral width was 5 KHz; pulse width 10 μs; acquisition time, 0.8 s; pulse delay, 3 s. Signal assignments were assisted by signal multiplicities obtained from SFORD or fully coupled spectra. Mass spectra were taken on AEI MS30 or RIBER MAG R-1010-C mass spectrometers. Silica gel refers to silica gel 60, 70—230 mesh (Merck). G.l.c. was performed on a Varian Aerograph 920 chromatograph (10 ft × ⅜ in column of 30% SE 30 on Chromosorb PAW 45—60 mesh) operating at 130 °C.

Oxidation of Phenols with Chlorous Acid: General Method.—A solution of sodium chlorite monohydrate (4 equiv.) in a minimum amount of water was added to a well stirred suspension of the appropriate phenol (*ca.* 0.3M) in 0.3M sulphuric acid cooled to 5 °C in an ice-bath. The mixture was stirred for 30 min and then degassed during 30 min under reduced pressure (water aspirator), while still being cooled in an ice bath.

For the analytical experiments, the aqueous phase was saturated with sodium chloride and extracted with ether. After being dried ($MgSO_4$), the solvent was removed, and the residue was dissolved in CD_3CN and directly analysed by ^{19}F n.m.r.

For product isolation, the aqueous phase was extracted successively with heptane, dichloromethane (ethanol free), and (after saturation with sodium chloride) with ether. The organic phases were dried over magnesium sulphate.

2-Chloro-2-trifluoromethylcyclopentene-1,3-dione (**3**).—After oxidation of phenol (**10**) (5 g), chromatography on silica gel (benzene) of the heptane extracts furnished compound (**3**) (81 mg). A further amount (86 mg) was obtained in the same way from the dichloromethane extracts (total yield 167 mg, 2.7%). The *dione* (**3**) had m.p. 55—56 °C (from CCl_4) (Found: C, 35.9; H, 1.0; Cl, 17.8; F, 28.1. $C_6H_2ClF_3O_2$ requires C, 36.3; H, 1.0; Cl, 17.9; F, 28.7%); $\nu_{max.}$(CCl_4) 1 745 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.65 (s); δ_F (56 MHz; $CDCl_3$) −71.5 p.p.m. (s); *m/z* 198 (M^+, 100%).

2-Trifluoromethyl-2,3-epoxy-p-benzoquinone (**9**).—Further elution with benzene of the heptane extracts of the preceding experiment gave the *epoxyquinone* (**9**) (202 mg, 3.4%), m.p. 24—25 °C (from hexane in the cold) (Found: C, 43.9; H, 1.55; F, 29.5. $C_7H_3F_3O_3$ requires C, 43.8; H, 1.6; F, 29.7%); $\nu_{max.}$(CCl_4) 1 705 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 4.15 (1 H, 3-H), 6.7 (2 H, 5- and 6-H); δ_F (56 MHz; $CDCl_3$) −73.2 p.p.m.; *m/z* 192 (M^+, 9%) and 69 (100).

5-Chloro-1-hydroxy-4-oxo-5-trifluoromethylcyclopent-2-enecarboxylic Acid (**4**).—The ether extracts from the experiment above were treated sequentially with acetonitrile and dichloromethane to remove the residual ether which is retained tenaciously, and were then allowed to crystallise in the cold (−30 °C) in dichloromethane. The *acid* (**4**) (3.86 g, 51%) was obtained in three crops as a white powder, m.p. *ca.* 100—105 °C (decomp.) (Found: C, 34.5; H, 1.6; Cl, 15.1; F, 23.3. $C_7H_4ClF_3O_4$ requires C, 34.4; H, 1.65; Cl, 14.5; F, 23.3%); $\nu_{max.}$(CH_3CN) 1 750, 3 400, and 3 650 cm^{-1}; δ_H (60 MHz; CD_3CN) 5.9 (2 H, OH), 6.68 and 7.69 (2 H, J_{AB} 6.1 Hz); δ_F (60 MHz; CD_3CN) −68.2 p.p.m.; *m/z* 200 ($M - CO_2$).

Bis[dimethyl(t-butyl)silyl] Derivative (**6**).—*N*-Methyl-*N*-dimethyl(t-butyl)silyltrifluoroacetamide (4 ml) was added *via* a syringe to the stirred powder acid (**4**) (1.0 g, 2.12 mmol) cooled in an ice-bath and under an inert atmosphere. The ice-bath was removed and the solution was stirred overnight. The solution was evaporated under reduced pressure (5 × 10^{-3} mmHg) and the residue distilled in a Buchi apparatus (oven temp. 170 °C; 6 × 10^{-3} mmHg) to give the *bis silyl derivative* (**6**) (1.77 g, 91%) as a white solid, m.p. 103.5—104 °C (Found: C, 48.1; H, 6.8; Cl, 7.7; F, 11.8; Si, 11.8. $C_{19}H_{32}ClF_3O_4Si_2$ requires C, 48.2; H, 6.8; Cl, 7.5; F, 12.05; Si, 11.9%); $\nu_{max.}$(CCl_4) 1 750 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 0.10 (3 H, Si*Me*), 0.12 (3 H, Si*Me*), 0.28 (6 H, SiMe_2), 0.86 (9 H, Si*Bu*^{t}), 0.90 (9 H, Si*Bu*^{t}), 6.54 and 7.53 (2 H, J_{AB} 6.1 Hz); δ_C (20 MHz; $CDCl_3$) −5.0 (Si*Me*), −3.2 (Si*Me*), 17.5 (*C*Me_3), 18.5 (*C*Me_3), 25.3 (Si*Bu*^{t}), 25.6 (Si*Bu*^{t}), 72.0 (C-3, J_{CF} 27.6 Hz), 88.0 (C-4), 121.8 (CF_3, J_{CF} 284.4 Hz), 133.4 (C-6), 160.3 (C-5), 167.0 (C-2), and 190.9 (C-7); δ_F (56 MHz; $CDCl_3$) −68.0 p.p.m.; *m/z* (DCI, NH_3) 490 ($M^+ + NH_4$, 100%); (e.i.) 415 ($M - C_4H_9$, 1%) and 73 (100).

Bis(trimethylsilyl) Derivative (**5**).—In the same way as above from the acid (**4**) (1.0 g) and bis(trimethylsilyl)trifluoroacetamide (2 ml) was obtained after distillation (oven temp. 110 °C; 7×10^{-3} mmHg) of the bis silyl derivative (**5**) (1.4 g, 95%); m.p. 44.5—46 °C. This compound is highly sensitive to moist air and no satisfactory analytical results could be obtained; $\nu_{max.}(CCl_4)$ 1 760 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 0.23 (9 H, $SiMe_3$), 0.29 (9 H, $SiMe_3$), 6.5 and 7.5 (2 H, J_{AB} 6.1 Hz); δ_C (20 MHz; $CDCl_3$) −0.6 ($SiMe_3$), 0.9 ($SiMe_3$), 73.6 (C-3, J_{CF} 25.7 Hz), 87.9 (C-4), 121.8 (CF_3, J_{CF} 282.6 Hz), 133.5 (C-6), 160.5 (C-5), 167.1 (C-2), and 190.5 (C-7); δ_F (56 MHz; $CDCl_3$) −68.8 p.p.m.; *m/z* 389 (*M* + 1, 0.4%) and 73 (100).

2-Chloro-1-hydroxy-3-oxo-2-trifluoromethylcyclopentanecarboxylic Acid (**7**).—An excess of triethylsilane (4 ml, 25 mmol) was added to a stirred solution of the acid (**4**) (2 g, 8.2 mmol) in trifluoroacetic acid cooled in an ice-bath. After 1 h the ice-bath was removed and the solution was stirred for 48 h. The solution was evaporated under reduced pressure (bath temp. 60 °C, 10^{-2} mmHg) and the residue was taken up in hexane and filtered to give the *saturated acid* (**7**) (1.65 g, 82%) as a white powder, m.p. 146.1—146.5 °C (from $CHCl_3$) (Found: C, 34.0; H, 2.4; Cl, 15.1; F, 23.3. $C_7H_6ClF_3O_4$ requires C, 34.1; H, 2.45; Cl, 14.4; F, 23.1%); $\nu_{max.}(CHCl_3)$ 1 750, 1 780, 2 600, 3 150, and 3 510 cm^{-1}; δ_H (60 MHz; CD_3CN) 2.1—3.1 (4 H, complex multiplet), 7.4 (2 H, 2 × OH); δ_C (20 MHz; CD_3CN) 31.5 (C-4 or C-5), 35.5 (C-4 or C-5), 72.6 (C-2, J_{CF} 26.6 Hz), 83.3 (C-1), 132.2 (CF_3, J_{CF} 283.2 Hz), 171.9 (CO_2H), and 201.5 (C-3); δ_F (60 MHz; CD_3CN) −67.0 p.p.m.; *m/z* (DCI, NH_3) 264 (*M* + NH_4, 40%) and 184 (100).

2-Chloro-3,3,3-trifluoropropanoic Acid (**19**).—After crystallisation of the acid (**4**), short-path distillation of the residue from the mother liquors (bath temp. 40 °C, 5×10^{-2} mmHg) afforded a crude product (550 mg) which was essentially the chlorinated acid (**19**), contaminated by traces of ether. A pure sample was obtained by g.l.c. The *acid* (**19**) had m.p. 26—27 °C (Found: C, 20.1; H, 2.1; Cl, 20.6; F, 32.5. $C_3H_2ClF_3O_2 \cdot H_2O$ requires C, 20.0; H, 2.2; Cl, 19.6; F, 31.6%); $\nu_{max.}$ (CCl_4) 1 740 and 3 000 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 4.73 (q, *J* 6.3 Hz), 10.3 (br, OH); δ_F (60 MHz; $CDCl_3$) −72.0 p.p.m. (d, *J* 6.3 Hz); *m/z* 117 (*M* − 45, 8%) and 98 (100).

Oxidation of the Phenol (**12**).—Oxidation of the phenol (**12**) was carried out as described on a 5 g scale. Since most of the starting material remained unconsumed, the crude product was reoxidised using the same conditions. Chromatography (SiO_2, CH_2Cl_2) of the heptane extracts afforded 2-chloro-4-trifluoromethylphenol (**13**) (550 mg, 9%) identical with an authentic sample.[16] In the same way careful chromatography of the dichloromethane extracts (SiO_2, CH_2Cl_2, ether gradient) afforded in order of elution: *2-chloro-4-hydroxy-4-trifluoromethylcyclohexa-2,5-dienone* (**15**) (334 mg, 5%), m.p. 68—69 °C (hexane) (Found: C, 40.2; H, 1.85; Cl, 16.7; F, 27.8. $C_7H_4ClF_3O_2$ requires C, 39.6; H, 1.9; Cl, 16.7; F, 26.8.%); $\nu_{max.}(CCl_4)$ 1 700 and 3 600 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 3.5 (1 H, OH), 6.47 (1 H, 6-H, $J_{6\text{-H},5\text{-H}}$ 9.9 Hz), 6.91 (1 H, 5-H, $J_{5\text{-H},3\text{-H}}$ 2.8 Hz), and 7.02 (1 H, 2-H); δ_F (60 MHz; $CDCl_3$) −79.7 p.p.m.; *m/z* 213 (*M* + 1, 3%), 212 (M^+, 3), and 143 (100); *4-hydroxy-4-trifluoromethylcyclohexa-2,5-dienone* (**14**) (249 mg, 4.5%), which had m.p. 86.5—87.5 °C (CCl_4) (Found: C, 47.3; H, 2.7; F, 32.2. $C_7H_5F_3O_2$ requires C, 47.2; H, 2.8; F, 32.0%); $\nu_{max.}(CCl_4)$ 1 685, 1 700, and 3 500 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 3.4 (1 H, OH), 6.4 and 6.9 (4 H, *J* 10 Hz); δ_F (60 MHz; $CDCl_3$) −79.7 p.p.m.; *m/z* 179 (*M* + 1, 34%), 178 (M^+, 26), and 109 (100).

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