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THALLIUM IN ORGANIC SYNTHESIS—XVI

PREPARATION OF *p*-QUINONES BY OXIDATION OF PHENOLS AND HYDROQUINONES WITH THALLIUM(III) TRIFLUOROACETATE[1,2]

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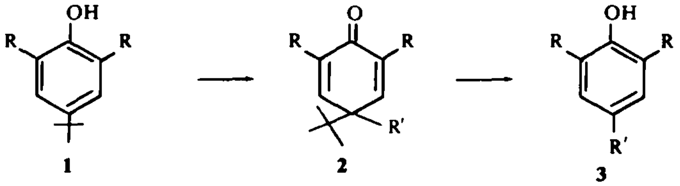
Abstract—Treatment of 2,6-disubstituted-4-t-butylphenols with thallium(III) trifluoroacetate in either trifluoroacetic acid or carbon tetrachloride as solvent results in loss of the 4-t-butyl substituent as isobutene and formation in high yield of the corresponding 2,6-disubstituted *p*-quinones. Possible mechanisms for this novel reaction, which probably proceeds *via* the intermediacy of a hydroquinone or hydroquinone mono-trifluoroacetate ester, are discussed. Consequent to these mechanistic considerations, thallium(III) trifluoroacetate is shown to be a highly efficient oxidant for the conversion of hydroquinones and a variety of 2,4,6-trisubstituted phenols into the corresponding *p*-quinones.

The potential utility of t-butyl substituted aromatic compounds in the synthesis of specifically substituted benzenoid derivatives has been recognised only during the last few years.[3-8] Much of the current interest in the chemistry of 4-t-butylphenols in particular is centred on the development of practicable procedures whereby these readily accessible compounds[9,10] can be converted into 4,4-disubstituted cyclohexadienones and thence, by loss of isobutene, into 4-substituted phenols (Chart 1).[11,12] Cyclohexadienones of the type **2** are normally prepared by treatment of the 4-t-butylphenol either with an appropriate nucleophile in the presence of a one-electron oxidizing agent[13-18] or, in certain specific cases, with electrophilic reagents.[19,20] Conversion of **2** into **3** can be achieved in high yield by the action of trifluoroacetic acid (TFA).[21]

CHART 1



We wish to describe in this paper an extension of the general transformation outlined in Chart 1, in which 2,6-disubstituted-4-t-butylphenols are converted directly and in high yield to the corresponding 2,6-disubstituted *p*-quinones on treatment with thallium(III) trifluoroacetate (TTFA).

The preparation of TTFA and its efficacy as a reagent in electrophilic aromatic thallation have recently been described.[22] Investigation of the scope of thallation with TTFA revealed that phenols reacted anomalously, oxidation of the aromatic substrate via formation and decomposition of aryloxythallium(III) di-trifluoroacetate intermediates generally preceding thallation.[23] Consequently it became apparent that, provided an appropriately substituted 4-t-butylphenol were employed, the overall transformation **1** → **3** might be accomplished in a single step by the action of TTFA in TFA.

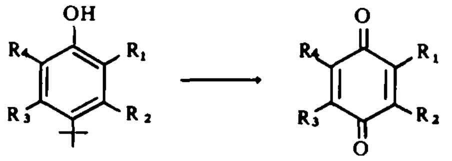
The validity of this hypothesis was tested using 2,4,6-tri-t-butylphenol as substrate. Treatment of this compound with a solution of one molar equivalent of TTFA in TFA at room temperature for one hour gave a mixture of products consisting of 2- and 4-t-butylphenol, 2,4-di-t-butylphenol, unchanged 2,4,6-tri-t-butylphenol, and an orange coloured solid, m.p. 65°. This latter compound, isolated in 30% yield, was easily identified as 2,6-di-t-butyl-*p*-quinone **10**. Consideration of possible mechanisms for its formation (*q.v.*) indicated that (a) two discrete oxidation reactions must be involved, and hence (b) use of two molar equivalents of TTFA should result in complete conversion of the phenol **4** to the quinone **10**. This proved to be the case: oxidation of **4** with two molar equivalents of TTFA proceeded smoothly and cleanly to give **10** in 73% yield. In addition, isolation of the quinone was considerably simplified due to the absence of phenolic compounds derived by proto-de-t-butylation of the starting material.

Investigation of the scope of this novel oxidation has established that it is a general reaction of 4-t-butylphenols in which the 2- and 6-positions are substituted by alkyl, aryl or halogen groups. Yield and experimental data for a number of typical conversions are summarized in Table 1. Use of TFA as solvent (Method A) results in rapid oxidation under homogeneous conditions and is generally the method of choice. Method B, oxidation by a suspension of solid TTFA in carbon tetrachloride, offers the attractive possibility of utilizing acid-sensitive substrates in this reaction, and should prove applicable to the synthesis of naturally occurring quinones.[23]

We suggest that the conversion of **4** into **10** is best explained by the reactions shown in Chart 2. Nucleophilic attack by trifluoroacetate anion on the initially formed intermediate **5** leads to the cyclohexadienone **6**, with concomitant reduction of Tl(III) to Tl(I). Reactive species analogous to **5** have been postulated previously in oxidations of phenols with lead (IV) acetate[24] and sodium bismuthate[25] in acetic acid, and thallium(III) oxide in ethanol.[26] Support for the intermediacy of **6** is found in the work of Hecker and Lattrell[27] who succeeded in isolating quinol ethers and acetates in low yield from the boron trifluoride catalysed reactions of certain *p*-alkylphenols with thallium(III) acetate in methanol and acetic acid respectively. Reduction of thallium in the manner shown is unexceptional;[26] facile reduction of Tl(III) to Tl(I) is well documented in the oxythallation reactions of olefins with thallium(III) acetate.[28, 29]

Acid catalysed elimination of isobutene[21] from **6** gives the hydroquinone monoester **7** from which, by one or both of two different routes, the quinone **10** may in turn be derived. Oxidations involving the use of standard solutions of TTFA in TFA almost certainly proceed via the hydroquinone **8**. Formation of **8** from **7** follows from the well established hydrolytic instability of trifluoroacetate esters[30, 31] and the presence in the reagent solution of stoichiometric amounts of water.* Oxidations with

TABLE 1. OXIDATION OF 4-*t*-BUTYPHENOLS TO *p*-QUINONES WITH TTFA



4-*t*-Butylphenol					*p*-Quinone			
					Yield, %[a]			
Index No	R_1	R_2	R_3	R_4	Method A[b]	Method B[c]	m.p. °C	Lit. m.p. °C
13	Br	H	H	Br	57	61	131	131–132[d]
14	Br	H	H	CH_3	89	83	94–95	94[e]
15	Br	H	H	t-C_4H_9	66	64	b.p. 176–182/35mm	*f*
16	Br	CH_3	H	t-C_4H_9	70	63	103–104	105[g]
17	Cl	CH_3	H	t-C_4H_9	67	72	92–93	94–95[g]
18	I	H	H	t-C_4H_9	87	57	b.p. 108–114/2mm	*h*
19	CH_3	H	H	CH_3	88	94	68–70	70–72[i]
20	t-C_4H_9	H	H	t-C_4H_9	73	88	65–66	67[j]
21	t-C_4H_9	H	H	C_6H_5	62	71	b.p. 110–115/2mm	*k*

[a] No attempt was made to optimise yields. [b] Oxidation by a solution of TTFA in TFA. [c] Oxidation by a suspension of anhydrous TTFA in carbon tetrachloride. [d] O. Heinichen, *Liebigs Ann.*, **253**, 267, (1889). [e] F. Kehrmann, *Chem. Ber.* **48**, 2021 (1915). [f] Found: C, 49·52; H, 4·81. $C_{10}H_{11}BrO_2$ requires: C, 49·48; H, 4·53%. [g] Ref. 19. [h] Satisfactory microanalytical data could not be obtained for this compound; NMR and IR spectral data, however, were fully consistent with the assigned structure. [i] L. I. Smith and B. Irwin, *J. Am. Chem. Soc.* **63**, 1036 (1941). [j] E. Müller and K. Ley, *Chem. Ber.* **88**, 601 (1955). [k] Found: C, 79·48; H, 7·01. $C_{16}H_{16}O_2$ requires: C, 79·97; H, 6·71%.

solid TTFA* in carbon tetrachloride (Method B) were, however, carried out under strictly anhydrous conditions. In these cases the quinone **10** most probably arises via formation of the cyclohexadienone **9** and subsequent elimination of trifluoroacetic anhydride.† It is of interest in this context that 4,4-dicarbalkoxy-2,5-cyclohexadienones (cf. **9**) have never been isolated. Treatment of 4-acetoxyphenols with a variety of oxidising agents in acetic acid, for example, has been shown to lead directly to the corresponding *p*-quinones, presumably via formation and decomposition of the diacetoxy derivatives analogous to **9**.[32]

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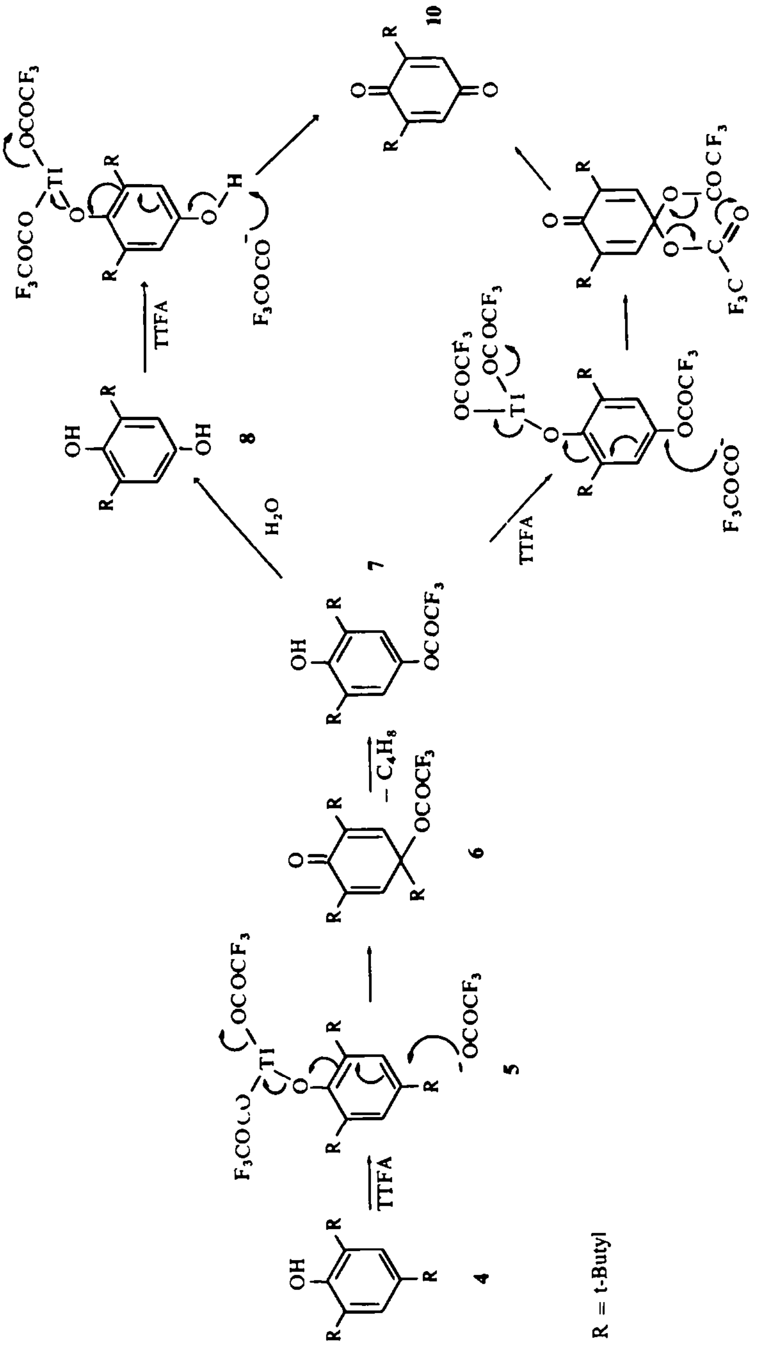
* Standard solns of TTFA in TFA were prepared by dissolving thallium(III) oxide in TFA. Removal of the water formed in this process is generally unnecessary. Anhydrous, crystalline TTFA is easily obtained, when required, by evaporation of the solution to dryness under reduced pressure.

† A similar cyclic mechanism has recently been postulated to account for the formation of duroquinone by pyrolysis of 1,4-dimethallyloxy-2,3,5,6-tetramethylbenzene (M. S. Newman and F. W. Hetzel, *J. Org. Chem.* **34**, 1216 (1969))

Chart 2



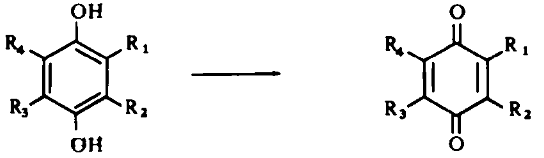
Attempts to isolate intermediates analogous to **5** and **9** during this oxidation have thus far proved unsuccessful. Indirect supporting evidence for the general scheme outlined in Chart 2 has, however, been obtained from a number of standard control reactions. Proto-de-t-butylation of t-butyl substituted aromatic compounds is a well known process,[33] and in the case of the phenol **4** could conceivably yield 2,6-di-t-butylphenol as product; plausible mechanisms for the conversion of this latter compound to the quinone **10** can be formulated. Treatment of **4** with TFA at room temperature for one hour did in fact result in extensive proto-de-t-butylation. 2,6-Di-t-butylphenol could not, however, be detected in the reaction mixture, which was composed of 2-t-butylphenol ($< 1\%$), 2,4,6-tri-t-butylphenol (4%), 4-t-butylphenol (20%), and 2,4-di-t-butylphenol (76%). In a separate experiment using 2,6-di-t-butylphenol, attempted oxidation with TTFA in TFA resulted only in extensive decomposition, and the quinone **10** could not be isolated from the reaction products. 2,6-Di-t-butyl-4-acetoxyphenol[34] on the other hand was oxidised to **10** smoothly and in high yield under identical conditions (cf. **7**).

Prior to the present work, oxidation of phenols and their derivatives with thallium reagents has received only scant attention. Mel'nikov and Gracheva found that thallium (III) chloride oxidized hydroquinone to a mixture of *p*-quinone and quinhydrone,[35] while Kabbe has claimed that conversion of hydroquinone to *p*-quinone is complete in three minutes when thallium(III) acetate is used.[36] The use of thallium-(III) oxide in ethanol for the oxidation of certain types of hydroquinone monoesters to *p*-quinones has recently been described.[26]

In contrast to the report by Kabbe, in our hands treatment of hydroquinone with thallium(III) acetate in acetic acid led initially only to quinhydrone; stirring of the reaction mixture at room temperature for 3 hr was necessary to effect complete oxidation to *p*-quinone.[37] The same reaction proceeded much more rapidly in TFA as solvent, *p*-quinone being formed in 79% yield in less than five minutes. When a solution of TTFA in TFA was employed, however, oxidation of hydroquinone to *p*-quinone required *less than one minute at room temperature.* Further aspects of this last reaction which were of particular interest were the total lack of decomposition products, the absence of any compounds arising from electrophilic thallation, and the experimental simplicity with which the pure quinone could be isolated from the reaction mixture (Experimental). Similar results were obtained with a variety of substituted hydroquinones, and experimental and yield data are listed in Table 2. As with those reactions involving 4-t-butylphenols, a variety of organic solvents may be used in conjunction with solid TTFA (Method B), and again carbon tetrachloride was found to be most satisfactory. The exceptional speed and manipulative simplicity of this technique thus recommend it as a valuable alternative to the more commonly applied methods for the oxidation of hydroquinones.[38]

That TTFA should efficiently oxidize hydroquinones and related compounds such as 4-aminophenols and 1,4-di-aminobenzenes to *p*-quinones is a logical consequence of the reaction sequence outlined in Chart 2. It is equally obvious, however, that oxidation of 2,4,6-trisubstituted phenols should not be restricted only to those compounds in which the 4-substituent is a t-butyl group. Decomposition of intermediates of the type **12** where X is a suitable leaving group such as halogen should also occur readily. This has been verified in practice, and details of representative conversions are given in Table 3. It is of interest that high yields of quinones are

TABLE 2. OXIDATION OF HYDROQUINONES TO *p*-QUINONES WITH TTFA

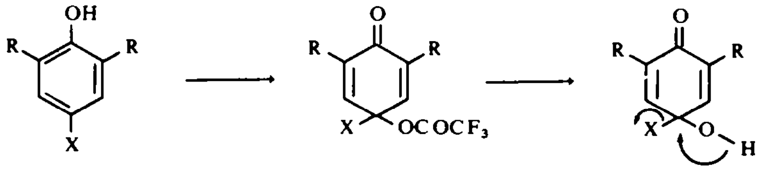


Hydroquinone					*p*-Quinone			
					Yield, %[a]			
Index No.	R_1	R_2	R_3	R_4	Method A[b]	Method B[c]	m.p. °C	Lit. m.p. °C
22	H	H	H	H	68	69	116	111–113[d]
23	CH_3	H	H	H	77	83	66–67	67–68[e]
24	t-C_4H_9	H	H	H	91	81	57–58	59[f]
25	C_6H_5	H	H	H	73	83	112–113	112–113[g]
26	Br	H	t-C_4H_9	H	63	—	108–110	*h*
27	t-C_4H_9	H	t-C_4H_9	H	94	93	149–150	150–151[i]
28	$C_2H_5C(CH_3)_2$	H	$C_2H_5C(CH_3)_2$	H	92	95	138–139	140[j]
29	CH_3	CH_3	CH_3	H	85	92	31	32[e]
30	Br	Br	Br	CH_3	94		234–236	233–235[k]
31	Cl	Cl	Cl	Cl	73	74	*l*	*l*

[a] No attempt was made to optimize yields. [b] Oxidation by a solution of TTFA in TFA. [c] Oxidation by a suspension of anhydrous TTFA in carbon tetrachloride. [d] *Organic Syntheses* Coll. Vol. II, p. 553. [e] E. Nölting and T. Baumann, *Chem. Ber.* **18**, 1150 (1885). [f] W. K. T. Gleim and A. Gaydash, U.S. Patent 2,573,136 (1951); *Chem. Abstr.* **46**, 3566 (1952). [g] F. Fichter and A. Sulzberger, *Chem. Ber.* **37**, 878 (1904). [h] Recrystallized from ethanol. Found: C, 49·11; H, 4·77. $C_{10}H_{11}BrO_2$ requires: C, 49·48; H, 4·53%. [i] A. Gurewitsch, *Chem. Ber.* **32**, 2424 (1899). [j] W. Koenigs and C. Mai, *Ibid.* **25**, 2649 (1892). [k] K. Auwers and R. F. v. Erggelet, *Ibid.* **32**, 3016 (1899). [l] Quinone sublimes; identity of synthetic material confirmed by comparison of IR spectrum with that of a genuine sample

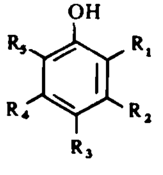
obtained in this last type of oxidation only when standard solutions of TTFA in TFA are employed. Attempted oxidations using a suspension of anhydrous TTFA in carbon tetrachloride or nitromethane as solvent led to gradual decomposition of the aromatic substrate, and the corresponding *p*-quinones were isolated in very low yields (< 5%). Presumably under these circumstances reaction proceeds only as far as the cyclohexadienone **11**, decomposition of which in a simple manner is not

CHART 3

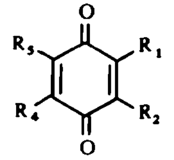


11 **12**

TABLE 3. OXIDATION OF MISCELLANEOUS PHENOLS TP *p*-QUINONES WITH TTFA/TFA



Phenol



p-Quinone

Index No.	R_1	R_2	R_3	R_4	R_5	Yield, %[a]	m.p. °C	Lit. m.p. °C
32	H	H	NH_2	H	H	88	115	111-113[b]
33	Br	H	NH_2	H	Br	81	131-132	131-132[c]
34	Br	H	Br	H	Br	77	131-132	131--132[c]
35	Br	H	Br	H	t-C_4H_9	81		[d]
36	Br	CH_3	Br	H	i-C_3H_7	94	43–45	47–48[e]
37	Br	CH_3	Br	H	t-C_4H_9	90	103	105[f]
38	Br	H	Cl	H	Cl	57	114–115	114–115[g]
39	Cl	H	Cl	H	Cl	82	119–120	121[g]
40	Cl	H	Cl	H	CH_3	80	88–89	90[h]
41	I	H	I	H	I	62	176--178	177–178[i]
42	t-C_4H_9	H	CH_3COO	H	t-C_4H_9	97	66	67[j]

[a] No attempt was made to optimize yields. [b] Footnote *d*, Table 2. [c] Footnote *d*, Table 1. [d] IR and NMR spectra identical to those of product obtained by oxidation of 2-bromo-4,6-di-t-butylphenol (Table 1). [e] F. Kehrmann, *Chem. Ber.* **22**, 3263 (1889). [f] Ref. 19. [g] A. R. Ling, *J. Chem. Soc.* **61**, 558 (1892). [h] A. Claus and H. Schweitzer, *Chem. Ber.* **19**, 927 (1886). [i] D. E. Kvalnes, *J. Am. Chem. Soc.* **56**, 667 (1934). [j] Footnote *j*, Table 1.

possible. In the absence of water hydrolysis to **12** can not take place, while decomposition by a cyclic elimination mechanism similar to that shown in Chart 2 for the transformation **9** → **10** is not apparently favoured. In support of these ideas, a 6–7 fold increase in the yield of quinone (to 30–40%) was observed in a number of instances when the calculated amount of water was added to the reaction mixture. Predictably, however, competitive hydrolysis of TTFA itself then occurred to a significant extent.* Use of a standard solution of TTFA in TFA is thus recommended for the oxidation of 2,4,6-trisubstituted phenols.

EXPERIMENTAL

M.ps were determined on a Kofler hot stage apparatus and are uncorrected. Microanalyses were performed by Mr. A. R. Saunders of the University of East Anglia. Where appropriate, identity of compounds was confirmed by comparison of IR spectra determined by the normal Nujol mull or liquid film techniques on a Perkin-Elmer Model 257 Grating Infrared Spectrophotometer.

Phenols. Compounds **13**, **20**, **22**-**25**, **27**, **29**, **31**-**34** and **39**-**41** were commercially available samples, and were purified prior to use. The following compounds were synthesized by literature procedures: **16**[19]

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* As much as 10–20% by volume of water can be added to solutions of TTFA in TFA before appreciable hydrolysis of TTFA takes place. Decomposition of the salt is rapid, however, when water is added to a suspension of the anhydrous solid in carbon tetrachloride or acetonitrile.

17,[19] **18**,[39] **19**,[40] **21**,[41] **28**,[42] **30**,[43] **35**,[44] **36**,[42] **37**,[19] **38**,[45] **42**.[34] The remaining compounds studied were prepared as described below.

2-Bromo-4-t-butyl-6-methylphenol, **14**, and *2-bromo-4,6-di-t-butylphenol*, **15**, were prepared by bromination of 4-t-butyl-2-methylphenol and 2,4-di-t-butylphenol respectively according to the general procedure described by Brown, Eglinton and Martin-Smith[44] *2-Bromo-4-t-butyl-6-methylphenol* was obtained in 70% yield as a pale yellow oil, b.p. 84–86°/0·6 mm (lit.[46] b.p. 94°/3 mm). *2-Bromo-4,6-di-t-butylphenol* was isolated in 97% yield as pale yellow needles, m.p. 51–53° after recrystallization from aqueous AcOH (lit.[46] b.p. 141–142°/7 mm).

2-Bromo-5-t-butylhydroquinone, **26**. A soln of 1·0 g (0·0062 mole) Br_2 in 2 ml AcOH was added to a mixture of 1·0 g (0·0057 mole) 2-t-butylhydroquinone and 1·0 g (0·012 mole) NaOAc in 20 ml AcOH and the pale yellow reaction mixture stirred at room temp for 30 min. *2-Bromo-5-t-butylhydroquinone* was not isolated, but was oxidized *in situ* to 2-bromo-5-t-butyl-*p*-quinone by addition of 2·5 g solid TTFA to the reaction mixture at this stage. The quinone was isolated by the general procedure described in the following experiment.

General procedures for the oxidation of 4-t-butylphenols with TTFA

Method A. The 4-t-butylphenol (0·05 mole) was added to a standard soln of TTFA in TFA[22] containing 0·11 mole TTFA, and the resulting deep red mixture stirred at room temp for 1–2 hr. The bulk of the TFA was then removed by evaporation under reduced press and the residue poured into 25–50 g ice-water. The quinone which separated at this stage was extracted with chloroform; the chloroform extracts were washed with water and then dried over Na_2SO_4. Concentration of the soln gave the crude quinone which was best purified by passage through a short column of silica gel using chloroform as eluent, concentration of the eluate, and crystallization or distillation of the product thus obtained.

Method B. Anhyd TTFA[22] (0·11 mole) was added to a sol of 0·05 mole 4-t-butylphenol in 25 ml dry CCl_4 and the mixture heated at 60–70° for 3–6 hr. The cooled mixture was filtered free from the thallium(I) trifluoroacetate which had precipitated, concentrated, and the crude quinone purified as described in Method A.

Treatment of 2,4,6-tri-t-butylphenol with TFA. 2,4,6-Tri-t-butylphenol (1·5 g) was stirred in 30 ml TFA at room temp for 1 hr. The bulk of the TFA was then removed by evaporation under reduced press and the residue dissolved in 30 ml ether. The ethereal soln was washed with $NaHCO_3$ aq and dried over Na_2SO_4. Removal of the solvent by evaporation under reduced press gave 0·6 g yellow oil which was analysed by GLC using a 2m Apiezon column and a Perkin–Elmer Model PE 452 Gas Chromatogram. Using genuine samples of each compound as both internal and external references, the components of the mixture were found to be 2-t-butylphenol, < 1%, 4-t-butylphenol, 20%, 2,4-di-t-butylphenol, 76%, and 2,4,6-tri-t-butylphenol, 4%.

General procedures for the oxidation of hydroquinones with TTFA

Method A. Addition of the hydroquinone (0·05 mole) to a standard soln of TTFA in TFA containing 0·11 mole TTFA resulted in almost instantaneous oxidation to the quinone. The mixture was generally stirred at room temp for 10–15 min to ensure completion of reaction, and the product then isolated using the general procedure described above in Method A for the oxidation of 4-t-butylphenols.

Method B. Anhyd TTFA (0·11 mole) was added to a soln of 0·05 mole hydroquinone in 25 ml dry CCl_4 and the mixture heated at 40–50° for 0·5–1 hr. Isolation and purification of the quinone were then carried out as described in method B for the oxidation of 4-t-butylphenols.

General procedure for the oxidation of miscellaneous phenols with TTFA

The phenol (0·05 mole) was added to a standard soln of TTFA in TFA containing 0·11 mole TTFA and the resulting mixture stirred at room temp for 6–10 hr. The pure quinone was obtained by the general procedure for isolation and purification described in Method A for the oxidation of 4-t-butylphenols.

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