Hydrogen Atom Transfers from Thiophenols to Triarylmethyl Radicals. Rates, Substituent Effects, and Tunnel Effects[1]

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Abstract: Rates of reaction between tris-*p-tert*-butylphenylmethyl radical and some substituted thiophenols are reported. The rate-determining step is $Ar_3C\cdot + HSAr' \rightarrow Ar_3CH + \cdot SAr'$; it is followed by the fast step $Ar_3C\cdot + \cdot SAr' \rightarrow Ar_3CSAr'$. Rates are also reported for Ar = Ph, Ar′ = Ph and 2,4,6-trimethylphenyl, where the trityl dimer dissociation rates must be considered. Substituent effects in Ar′ are not large, covering a range of less than a factor of 20 at 0 °C. The rate constants do not correlate with ordinary substituent constants, although a modestly good correlation with the Taft σ_R suggests that polar contributions are small, and the rate differences arise from differences in the product Ar′S·. Large variations are unexpectedly found in the preexponential factor (from about 1×10^7 to 3×10^9). They correlate with activation energy and are shown to be attributable to substantial variation in the tunnel correction. A rough model calculation shows that the effects are not unreasonable. The tunnel correction varies considerably because there is a substituent effect on the endothermicity of the rate-determining step.

In a previous paper,[3] measurements were reported on the equilibrium between the triphenylmethyl radical and its dimer, as well as the rate of hydrogen abstraction from thiophenol. This clearly showed the feasibility of determining absolute rates and Arrhenius parameters for these hydrogen atom transfer reactions. Since few absolute rates of hydrogen atom transfers have been measured except by experimentally complex fast reaction methods or by competitive comparison with a previously determined absolute rate,[4] it was decided to investigate the reaction of a series of substituted thiophenols. Of particular interest was a possible comparison with the conclusion drawn from earlier isotope effect work from this laboratory.[5]

It was first considered necessary to reinvestigate the reaction of the trityl radical with thiophenol, because the sample cell in the apparatus used in the previous equilibrium and rate measurements was found to retain an appreciable amount of liquid when it was emptied. Since the cell was filled and emptied several times before each determination, this retention would not affect equilibrium constant measurements, but could affect the kinetic work. A manual syringe was added to the system to allow the cell to be rinsed with pentane and then dried after each use. The new results are presented in Table I. The rate constants are adequately fit by the Arrhenius equation.

$$k = 6.96 \times 10^{7 \pm 0.142} \exp(-9540 \pm 180 \text{ cal mol}^{-1}/RT) \tag{1}$$

These results differ somewhat from the original report,[3] which gave $A = 2.65 \times 10^7$, $E_a = 9060$ cal/mol; the difference is attributable to the incomplete emptying of the cell in the earlier work. This dilution of the reagents would lower the apparent rate constants. In accordance with this, the rates reported in this work are larger at all temperatures than those in the previous work by about 20%.

The reaction of the trityl radical with 2,4,6-trimethylbenzenethiol was also investigated. The results are given in Table II and can be reproduced with good precision by the equation

$$k = 3.13 \times 10^{7 \pm 0.091} \exp(-8910 \pm 130 \text{ cal mol}^{-1}/RT) \tag{2}$$

The hydrogen atom is abstracted from thiophenol or 2,4,6-trimethylbenzenethiol at a rate comparable to that for the establishment of the trityl radical dimerization equilibrium, so calculation of the rate constants for the reaction of the trityl radical required values for the dissociation and recombination rate constants for this equilibrium. Ziegler's literature values[6] for the dissociation rate constants were used, but these were only measured between −20 and 10 °C. Values for temperatures greater than 10 °C were obtained from the Arrhenius parameters calculated from Ziegler's data. An Arrhenius plot of this data is curved below −5 °C, so only the rates measured at −5, 0, 5, and 10 °C were used to derive the Arrhenius parameters. Extrapolation to the temperatures used for the kinetic work with the trityl radical reported here should be acceptable, but it is a potential source of error. Also, a systematic error is possible if the temperature scales of Ziegler and our systems do not coincide. Finally, the computational procedure used to obtain the rate constants is tedious: it requires significant amounts of computer time and real time, and requires visual curve fitting.

Since these problems are due to the equilibrium between the trityl radical and its dimer, we switched to the tris-*p-tert*-butylphenylmethyl radical, which has been shown to be 100% dissociated in solution.[7] Replacement of the three para hydrogens of the trityl radical by bulky *tert*-butyl groups,[8] nitro groups,[9] or phenyl groups[10] prevents dimerization, presumably owing to steric hindrance. However, the tris-*p*-xenylmethyl radical is reported to be extremely acid sensitive[11] and three *p*-nitro groups may greatly alter the reactivity of the trityl radical,[12] so we chose the tris-*p-tert*-butylphenylmethyl radical.

The reaction of the radical with the thiols can be written as

$$Ar_3C\cdot + Ar'SH \xrightarrow{k_1} Ar_3CH + Ar'S\cdot$$

$$Ar_3C\cdot + Ar'S \xrightarrow{k_2} Ar_3CSAr' \tag{3}$$

The assumption of a steady-state concentration of thiyl radicals and integration of the expression for the disappearance of the radical leads to the integrated second-order rate equation:

$$\{1/(2Ar'SH_0 - R_0)\} \times \ln\{R_0(2Ar'SH_0 - R_0 + R)/2RAr'SH_0\} = k_1 t \tag{4}$$

where R is the concentration of radical at time t, and $Ar'SH_0$ and R_0 are the initial concentrations of the thiol and the radical. Since only solutions of the radical were used, and the concentration is required, it was necessary to measure the extinction coefficient of the radical to convert absorbance to

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Table I. Rate Constants for the Reaction of Thiophenol with the Triphenylmethyl Radical in Toluene

t, °C	k,[a] exptl	k,[b] calcd
41.1	15.9	16.2
19.2	5.6	5.2
10.9	3.08	3.2

[a] $M^{-1}\ s^{-1}$; average of five independent determinations. [b] $M^{-1}\ s^{-1}$; calculated from eq 1.

Table II. Rate Constants for the Reaction of 2,4,6-Trimethylbenzenethiol with the Triphenylmethyl Radical in Toluene

t, °C	k,[a] exptl	k,[b] calcd
41.89	20.8	20.6
29.87	11.5	11.7
19.6	7.0	7.0
11.0	4.4	4.4

[a] $M^{-1}\ s^{-1}$; average of eight independent determinations. [b] $M^{-1}\ s^{-1}$; calculated from eq 2.

Table III. Rate Constants for the Reaction of the Tris-*p*-*tert*-butylphenylmethyl with Substituted Thiophenols in Toluene

substituent on thiophenol	t, °C	k, exptl[a]	k, calcd[b]
none	41.6	28.5	28.2
none	31.6	20.0	17.4
none	25.0	11.18	12.4
none	12.1	5.74	6.11
none	−1.9	2.70	2.63
p-Cl	39.9	51.4	54.7
p-Cl	30.4	33.0	32.5
p-Cl	9.6	10.3	9.20
p-Cl	0.27	5.0	4.91
p-Cl	−8.5	2.50	2.61
p-*t*-Bu	25.25	12.9	13.2
p-*t*-Bu	10.75	5.02	5.19
p-*t*-Bu	0.58	2.57	2.54
p-CF_3	21.1	9.46	8.72
p-CF_3	9.55	3.92	3.91
p-CF_3	0.20	1.90	1.94
p-CF_3	−9.09	0.94	0.92
m-Cl	41.1	45.0	43.4
m-Cl	31.1	24.1	25.4
m-Cl	20.0	13.6	13.4
m-Cl	9.8	7.57	7.09
m-Cl	−0.4	3.45	3.58
m-Cl	−7.8	2.00	2.11
p-OMe	30.5	65.0	66.8
p-OMe	20.0	44.4	43.9
p-OMe	10.4	28.2	28.8
p-OMe	0.70	18.4	18.2

[a] $M^{-1}\ s^{-1}$; average of about six independent determinations. [b] $M^{-1}\ s^{-1}$; calculated from Arrhenius parameters of Table IV.

Table IV. Arrhenius Parameters for the Reaction of the Tris-*p*-*tert*-butylphenylmethyl Radical with Substituted Thiophenols in Toluene

substituent on thiophenol	$E_a{}^{*}$[a]	A^{*}[b]
p-OMe	7.28 ± 0.21	$1.17 \times 10^{7 \pm 0.164}$
none	9.25 ± 0.23	$7.46 \times 10^{7 \pm 0.174}$
m-Cl	10.25 ± 0.11	$5.88 \times 10^{8 \pm 0.081}$
p-Cl	10.35 ± 0.16	$9.20 \times 10^{8 \pm 0.121}$
p-*t*-Bu	10.88 ± 0.16	$1.23 \times 10^{9 \pm 0.125}$
p-CF_3	11.49 ± 0.20	$2.99 \times 10^{9 \pm 0.158}$

[a] kcal mol^{-1}. [b] $M^{-1}\ s^{-1}$.

concentration. Equation 5 may be derived using the stoichiometry of the reaction:

$$\epsilon = \frac{A_1V_1 - A_2(V_1 + V_t)}{2V_tC_t} \tag{5}$$

where A_1 and V_1 are the absorbance and volume of solution in the cell before addition of the thiol solution, A_2 is the absorbance after the reaction with the added thiol is over, V_t is the volume of added thiol solution, and C_t is the concentration of the thiol solution being added. This equation was used to calculate the extinction coefficient of the radical from a number of kinetic runs with several of the thiols and gave ϵ = 750 ± 20 at the 525-nm maximum of the radical absorbance.[11] A small correction for the reaction of the radical with residual oxygen in the cell compartment was applied to the kinetic runs as well as the extinction coefficient measurements.

The thiols studied were the parent and those with *p*-Cl, *p*-*t*-Bu, *p*-CF_3, *m*-Cl, and *p*-OCH_3 substituents. All gave satisfactorily linear plots corresponding to eq 4, indicating that they all react as in eq 3. Furthermore, product studies were performed for the reaction of the tris-*p*-*tert*-butylphenylmethyl radical with *p*-methoxythiophenol, which reacted the fastest at all temperatures, and thiophenol, which was one of the slowest reacting thiols. In both cases, only the expected triarylmethane and the triarylmethyl aryl sulfide were isolated. The results of the kinetic studies for all of the thiols are given in Table III. Arrhenius plots for all of the data for each thiol, not just the average values given in Table III, gave the Arrhenius parameters listed in Table IV. The estimated errors are the standard deviations of the coefficients for the fit of a least-squares line to the data by a standard computer program. Comparison of the calculated rates to the average rates at the various temperatures in Table III shows that the Arrhenius plots are all acceptably linear.

Discussion

These results constitute some of the very few available rates of good precision for hydrogen atoms transfers involving carbon radicals. The initial aim was to attack the problem of substituent effects on hydrogen abstraction rates and to assess the relative importance of product stabilities and the possible contribution of polar structures to the transition state.[13] In the attack of various radicals on toluene, the sign and magnitude of the Hammett ρ has been used to give information on this point.[13,14] Interpretation of the present data in terms of ρ is impossible, since the correlation with either σ or σ^+ is very poor. There is, however, a modest correlation with Taft's σ_R,[15] suggesting that resonance in the product thiyl radical is more important than special inductive transition state effects.

Such an interpretation is open to criticism because of the very large variation in the preexponential factors, and the correlation of the log A^* terms with the $E_a{}^*$ terms. This is in fact roughly linear and leads to an isokinetic temperature[16] of 99 °C. Thus, unless we can show that the Arrhenius plots cannot be reliably extrapolated even this far, the substituent effects would be reversed above this temperature. We propose to show that the variation in A^* is a consequence of significant tunnel corrections, which indeed can be expected to disappear at slightly higher temperatures. Thus, the correlation with σ_R is at least qualitatively correct at all temperatures.

The necessary substituent-dependent tunnel corrections are a consequence of the endothermicity[17] of all the reactions and a dependence of tunnel correction on symmetry (ΔH) exactly analogous to that proposed by Bell, Sachs, and Tranter[18] for proton transfers. These are conveniently illustrated by a model calculation which shows the effect on A^*, but does not relate the model rigorously to the data.

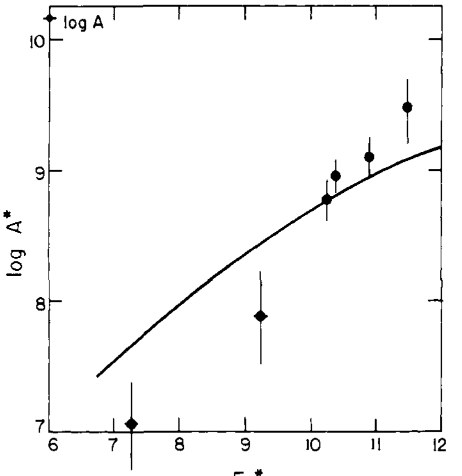

Figure 1. Curve: plot of log A^* vs. E_a calculated as described in the text for $A = 1.5 \times 10^{10}$, $a = 0.45$ Å, $b = 0.5$, $c = 10.4$ kcal/mol, $t = 273$ K. Points are the experimental points from Table IV, shown with 2σ error bars in log A^*. The points do not fit the curve, but are qualitatively related.

Table V. Consequences of Tunnel Correction Calculated from Bell's Truncated Parabola Barrier at 273 K with $a = 0.45$ Å

E^a	u	Q^b	A^*/A^b	$(E_a - E_a{}^{*b})^a$
10	5.69	9.7[c]		
9.5	5.54	7.7	2.2×10^{-3}	4.4
9	5.40	6.3	7.9×10^{-3}	3.1
8	5.09	4.5	4.0×10^{-2}	2.6
7	4.76	3.4	1.0×10^{-1}	1.9
6	4.41	2.7	2.0×10^{-1}	1.4
5	4.02	2.2	3.2×10^{-1}	1.1

[a] kcal mol^{-1}. [b] Using eq 6, the first term of Bell's equation. [c] Overestimated by neglect of higher terms in Bell's equation, these cannot be included without losing the simple analytic expressions for the A^* and $E_a{}^*$; the value of Q using two terms is 8.3.

The tunnel correction Q is given to a first approximation in Bell's[19] truncated parabolic barrier model by

$$Q = (u/2)/\sin(u/2) \qquad (6)$$

in which u depends on the height of the barrier, E, its width, $2a$, the reduced mass, m, of the imaginary vibration of the activated complex, and the temperature T, as given in the equation

$$u = hE^{1/2}/\pi a(2m^{1/2})kT \qquad (7)$$

We shall for simplicity assume that a is a constant and m is a constant 1 amu. The effect of tunneling on the apparent Arrhenius constants A^* and $E_a{}^*$ is given by

$$A^*/A = \exp[\ln Q + (u/2)\cot(u/2) - 1] \qquad (8)$$

$$E_a{}^* - E_a = kT[(u/2)\cot(u/2) - 1] \qquad (9)$$

where A and E_a (without asterisks) refer to the classical terms, either as a theoretical concept or as a high-temperature limit of A^* and $E_a{}^*$.

It is also necessary to use a relation between E_a and ΔH; we adopt the simplest, the Polanyi linear relation[20]

$$E_a = c + b\Delta H \qquad (10)$$

with $b = 0.5$. Parenthetically, we should note that a more general or broadly applicable expression, such as that of Marcus,[21] or the hyperbolic relation,[22] $E_a(E_a - \Delta H) = c^2$, changes E_a less than 5% over the range that we shall use below. Bell, Sachs, and Tranter used the Marcus quadratic expression, which also differs little.

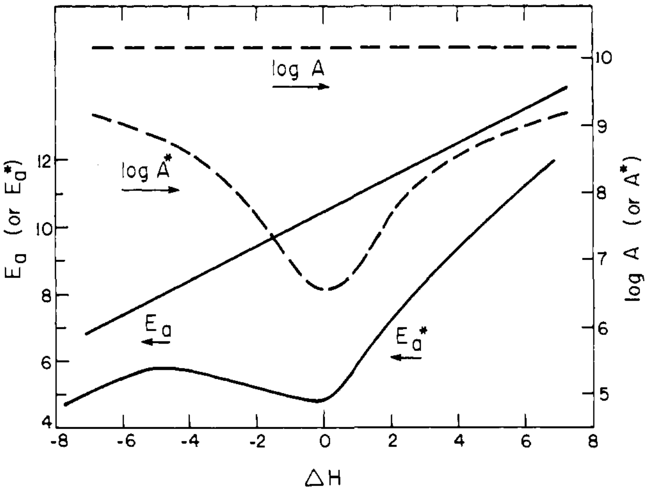

Figure 2. Solid line: calculated plot of $E_a{}^*$ and E_a vs. ΔH. Dashed line: plots of A and A^* vs. ΔH. The curve is only qualitative in the neighborhood of $\Delta H = 0$, but is otherwise calculated from Table V and the value $c = 10.4$ (eq 6–9) and $A = 1.5 \times 10^{10}$. Note how the curve for $E_a{}^*$ goes through a maximum for negative ΔH, making a correlation of log A^* with E_a unlikely in this region.

The reactions are all endothermic and the barrier in eq 7 is the barrier for the reverse reaction, since reacting systems with energies less than the product cannot tunnel, but the tunnel correction for forward and reverse reactions must be identical. Thus $E = c - 0.5\Delta H$ for positive ΔH.

Selecting quite arbitrarily $a = 0.45$ Å and using $T = 273$ K, the items sensitive to tunneling for various E are given in Table V.

It can be seen that the range of A^*/A between $E = 9.5$ and $E = 7$ is not far from that observed experimentally. We can therefore see if the other data can be approximated. If we choose $c = 10.4$ kcal/mol as the value of E_a for $\Delta H = 0$ and $A = 1.5 \times 10^{10}$, then this range covers A from 1.4×10^9 to 3.2×10^7. Using the readily derived equation (depending on $b = 0.5$) $E_a = 2c - E$, this range also corresponds to E_a varying from 11.3 to 13.8, and, using the last column of Table V, $E_a{}^*$ would thus vary from 6.9 to 11.9 kcal/mol. The relation is shown in Figure 1, which is a plot of log A^* vs. $E_a{}^*$; the experimental points are also shown. The plot is of course not a linear plot, although it does not deviate from linearity by any likely experimental error. The values of ΔH imposed by the choice of c and the range of E are from +1.8 to +6.8 kcal/mol, but Figure 2 shows a plot of $E_a{}^*$ vs ΔH covering a larger range of ΔH of both signs, and also a plot of log A^*/A vs. ΔH. The plot is based on the above model, but curves of a similar form will result from any calculation which has an E_a rising smoothly with ΔH, and in which the wide-range Arrhenius plot is concave upward because of the tunnel correction.

It is clear that tunnel corrections within the range of those previously observed can produce a correlation of $E_a{}^*$ and A^* for a series of endothermic reactions of constant A factor covering the range observed. A fit within experimental error of these limited data by suitable adjustment of the various parameters, i.e., a, b, c, the range of ΔH, A, as well as choice of the form of tunnel correction is quite possible; we refrain from doing it, for it would give greater significance to the values of the chosen parameters than they deserve. Perhaps the most important modification of the above calculations would be to introduce a variation in a, and also to account for an increase in m in the less symmetrical cases.

We should briefly discuss the question of whether there is an alternative explanation of the results. Correlations of E_a and A are frequently the result of experimental error.[23] We believe that our error estimates on $E_a{}^*$ and A^* are realistic and

Table VI. Calculated Isotope Effects for the Reaction of the Trityl Radical with 2,4,6-Trimethylbenzenethiol in Toluene

t, °C	k_H/k_T, exptl[a]	k_H/k_T, calcd[b]
0.0	41.4	40.5
8.0	35.0	33.7
15.0	30.5	29.3
25.0	25.3	24.5
32.0	22.3	22.0
40.0	19.5	19.6

[a] From ref 28. [b] Calculated with $E^H{}_{\text{class}}$ = 11.1 kcal mol^{-1}, $E^T{}_{\text{class}}$ = 12.5 kcal mol^{-1}, and a = 0.52 Å.

find it unreasonable that A^* is not in fact varying considerably. Exner's[16] criterion for statistical significance of a plot of $k_{30\,°C}$ vs. $k_{0\,°C}$ (each evaluated by interpolation from points at nearby temperatures from Table III) also shows a correlation, similar to that of E_a^* vs. log A^*. Effects arising from the formation of hydrogen-bonded dimers are not significant; not only are the kinetic plots linear down to virtually complete disappearance of thiol, but published results suggest that there is little dimerization of the thiols at the concentrations used (less than 0.0014 M).[24] Solvation effects causing variation in A should not be important for the reaction of electrically neutral species in a nonpolar solvent.[25] The assumption of constant A is based on a considerable mass of data; for example, in the gas phase the preexponential factor for attack of methyl radicals on hydrocarbons depends principally on the number of equivalent hydrogens.[4b,26]

The suggestion of tunneling in these reactions is not new; the A_H^*/A_T^* ratio is 0.187[27] for the reaction of the trityl radical with thiophenol and tritiated thiophenol, and for the reaction with mesityl mercaptan A_H^*/A_T^* is 0.114.[28] In these cases, small A_H^*/A_T^* factors were taken to indicate tunneling. Caldin[29] has reported barrier dimensions calculated from isotope effect data for proton transfers, based on the equations from Bell's truncated parabolic barrier model. A similar calculation for the tritium isotope effects for the hydrogen atom transfer from mesityl mercaptan to the trityl radical gave the best fit to the experimental data with a = 0.52 Å, E^H = 11.1, E^T = 12.5 kcal mol^{-1} as shown in Table VI. These values give at 25 °C Q_H = 3.4, within the range of those in Table V. It should be noted that it is no longer necessary to attribute this substantial tunnel correction to a steric effect, as originally postulated.[28]

We conclude first that the substituent effects on these reaction rates are principally determined by varying resonance stabilization of the product thiyl radicals. Second, tunnel corrections are important for the *p*-methoxythiophenol case and much less so for the *p*-trifluoromethyl case, and are manifested by reduced E_a^* and A^* apparent Arrhenius terms. Third, this reduction and variation in A^* factors in the series where constant A factors are expected constitutes a new criterion for tunneling independent of isotope effects or of detectably curved Arrhenius plots.

Experimental Section

^{1}H NMR spectra were obtained on a Varian A-56 60 or Varian EM-390 spectrometer with tetramethylsilane as internal reference. Melting points were determined on a Fisher-Johns melting point apparatus. Both melting points and boiling points are uncorrected. The apparatus and method described previously,[3] with the changes discussed in this paper, were used to determine all of the rate constants reported here. All of the thiols were purified by triple distillations under an argon atmosphere. Thiophenol (Aldrich), *p*-chlorothiophenol (Aldrich), and *m*-chlorothiophenol (Pfaltz and Bauer) were commercially available.

Materials. 2,4,6-Trimethylbenzenethiol, *p*-methoxythiophenol, and *p-tert*-butylthiophenol were prepared by the procedure of Cohen and Wang[30] for the synthesis of 2,4,6-trimethylbenzenethiol. 2,4,6-Trimethylbenzenethiol: bp 78-80 °C (10 mm) (lit.[30] 227-229 °C (760 mm)); ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 2.07 (s, 6 H), 2.72 (s, 1 H), 6.43 (s, 2 H). *p*-Methoxythiophenol: bp 83 °C (4 mm) (lit.[31] 227-229 °C); ^{1}H NMR ($CDCl_3$) δ 3.30 (s, 1 H), 3.66 (s, 3 H), 6.93 (distorted quartet, 4 H). *p-tert*-Butylthiophenol: bp 118-119 °C (20 mm) (lit.[32] 120 °C (20 mm)); ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H), 3.21 (s, 1 H), 7.1 (s, 4 H).

p-Trifluoromethylthiophenol was prepared by an adaptation of the procedure for the preparation of *m*-trifluoromethylthiophenol.[33] Concentrated hydrochloric acid (93 mL) and 160 g of ice were added to a 1-L three-neck flask equipped with an addition funnel, mechanical stirrer, and reflux condenser. The flask was cooled in an ice-salt bath and 50 g of *p*-trifluoromethylaniline (Aldrich) was slowly added. A solution of 23.6 g of sodium nitrite in 50 mL of deionized water was added dropwise with stirring. In a separate 2-L three-neck flask equipped with a mechanical stirrer, an addition funnel, and a reflux condenser were placed 68.3 g of potassium hydroxide and 62.1 g of ethylxanthic acid potassium salt (Eastman) in 80 mL of water. This flask was heated to 40-45 °C (in an oil bath) and the cold diazonium solution was slowly added (Note: It is important to maintain the oil bath above 40 °C. Violent explosions have been reported for xanthate ester formation below this temperature.)[34] After the addition was complete, the solution was stirred for an additional 30 min, cooled, and extracted with ether. The ether solution was dried over magnesium sulfate and the ether removed on a rotary evaporator. The residual oil was dissolved in 300 mL of 95% ethanol and heated to reflux. Potassium hydroxide (93.1 g) was slowly added and the solution refluxed overnight. The next morning, the solution was made strongly acidic with 6 N sulfuric acid. It was placed in a 3-L flask and steam distilled in the presence of 2 g of zinc powder. Separation of the organic layer and distillation gave *p*-trifluoromethylthiophenol: bp 53.5-54 °C (10 mm) (lit.[35] 60-61 °C (13 mm)); ^{1}H NMR ($CDCl_3$) δ 3.50 (s, 1 H), 7.30 (distorted quartet, 4 H). It was found that distillations at temperatures above 100 °C (25 mm or more) led to significant decomposition of the *p*-trifluoromethylthiophenol.

***p-tert*-Butylbromobenzene.** *tert*-Butylbenzene (225 g) and 4 g of iron powder were placed in a three-neck round-bottom 2-L flask equipped with a reflux condenser, addition funnel, and mechanical stirrer, and cooled in an ice bath: then 300 g of bromine was added dropwise with stirring. The stirring was continued for 3 h after the addition was complete. The mixture was put in a separatory funnel and washed with water, 5% sodium sulfite, twice with 5% sodium carbonate, and twice with water. The organic layer was dried over magnesium sulfate and distilled to give 400 g (75%) of *p-tert*-butylbromobenzene: bp 90 °C (5 mm) (lit.[36] 103 °C (10 mm)); ^{1}H NMR ($CDCl_3$) δ 1.3 (s, 9 H), 7.37 (distorted quartet, 4 H).

Tris-*p-tert*-butylphenylcarbinol. Magnesium (30 g) and a small amount of ether were placed in a dried 2-L three-neck round-bottom flask equipped with a stirrer, reflux condenser, and addition funnel with a nitrogen inlet. A small portion of *p-tert*-butylbromobenzene and a crystal of iodine were added to start the reaction. A solution of 220 g of *p-tert*-butylbromobenzene in 250 mL of ether was then added at a rate to maintain reflux. After the addition was complete, the solution was refluxed for 1.5 h and then 30.8 g of dimethyl carbonate in 100 mL of ether was added dropwise with stirring. The solution was refluxed for 1 h and then poured over ice and hydrochloric acid. The ether layer, along with three ether extractions of the aqueous phase, was washed three times with water, twice with 5% sodium carbonate, and three more times with water. The solution was dried over sodium sulfate and the ether removed on a rotary evaporator to yield a tan slurry of the carbinol which was not isolated but used in an impure form.

Tris-*p-tert*-butylphenylmethyl Chloride. Freshly distilled acetyl chloride was added to the crude tris-*p-tert*-butylphenylcarbinol and the mixture refluxed overnight. The greenish slurry was filtered and the crystals were added to fresh acetyl chloride; the crystals were washed with petroleum ether, placed in a vacuum desiccator, and dried for several days. The desiccator was placed in a glovebag which was purged six times with dry nitrogen. The desiccator was opened and the white, crystalline chloride was placed in sealed ampules for storage. A weighed sample of the chloride was dissolved in 95% ethanol: titration with standard base showed the chloride to be greater than 98% pure.

Tris-*p-tert*-butylphenylmethyl Radical. The desired amount of tris-*p-tert*-butylphenylmethyl chloride was dissolved in purified toluene. A tenfold excess of molecular silver and a magnetic stirring bar were added. (It was found that mercury, which was used for the preparation of the trityl radical,[3] gave a reproducible low conversion of the chloride to the radical, while molecular silver gave a high yield of the radical. Although the conversion may not be quantitative even with silver, separate experiments showed that the tris-*p*-*tert*-butylphenylmethyl chloride reacts very slowly with thiophenols in toluene; thus incomplete reduction will not interfere.) The flask was then evacuated and wrapped with foil. The solution was stirred magnetically for several hours, and the flask was placed in a glovebag. After the glovebag was purged with argon at least ten times, the flask was opened and the solution filtered to remove excess silver and silver chloride. The toluene solution of the radical could then be placed in the refill reservoir for the delivery system.[3]

Molecular Silver. Two procedures were employed and no difference was noted in the reactivity of the silver produced.

Procedure A.[37] Freshly prepared silver chloride was placed in a clean evaporating dish and covered with deionized water. A small amount of zinc chloride was added to the solution. A platinum grid was placed on one side of the dish and connected via an ammeter to a large extraction thimble filled with pieces of zinc rod and zinc powder on the other side. When the ammeter indicated that little current was flowing (5 or 6 days), the silver was collected and washed with water, ammonium hydroxide, water, 95% ethanol, absolute ethanol, ether, benzene, and petroleum ether. It was then placed in a vacuum desiccator and dried for several days.

Procedure B.[38] Freshly prepared silver chloride was dissolved in concentrated ammonium hydroxide. An equimolar amount of cuprous chloride was dissolved in concentrated ammonium hydroxide and slowly added to the silver chloride solution with stirring. The solution became deep blue and the precipitated silver was collected and washed as in procedure A.

Tris-*p*-*tert*-butylphenylmethane. An 87.3-g portion of 5% sodium amalgam, 4.78 g of tris-*p*-*tert*-butylphenylmethyl chloride, and 115 mL of ether were placed in a 250-mL Erlenmeyer flask and shaken for 6 h. The solution was filtered to remove sodium chloride and mercury, shaken with ethanol, and then washed three times with water. The solution was dried over magnesium sulfate and the ether removed on a rotary evaporator. After three recrystallizations from absolute ethanol, the solid had mp 174–175 °C; ^1H NMR ($CDCl_3$) δ 1.27 (s, 27 H), 5.38 (s, ^1H), 7.11 (distorted quartet, 12 H). Anal. ($C_{31}H_{40}$) C, H.

Tris-*p*-*tert*-butylphenylmethyl Phenyl Sulfide.[39] Equimolar amounts of tris-*p*-*tert*-butylphenylmethyl chloride and thiophenol were dissolved in warm glacial acetic acid. Concentrated sulfuric acid was added, and an oil separated which crystallized upon cooling. Three recrystallizations from ethanol gave mp 158–159 °C; ^1H NMR ($CDCl_3$) δ 1.25 (s, 27 H), 6.73 (s, 5 H), 7.04 (s, 12 H).

Tris-*p*-*tert*-butylphenylmethyl *p*-Methoxyphenyl Sulfide. Tris-*p*-*tert*-butylphenylmethyl chloride (5 g), 1.6 g of *p*-methoxythiophenol, and 0.64 g of potassium hydroxide were placed in a 100-mL round-bottom flask with 60 mL of absolute ethanol and refluxed for 2 h. The solution was cooled and filtered. Three recrystallizations from ethanol gave mp 182–183 °C; ^1H NMR ($CDCl_3$) δ 1.27 (s, 27 H), 3.67 (s, 3 H), 6.63 (distorted quartet, 4 H), and 7.20 (distorted quartet, 12 H).

Product Studies for Tris-*p*-*tert*-butylphenylmethyl Radical Reaction with Thiophenol and *p*-Methoxythiophenol. The tris-*p*-*tert*-butylphenylmethyl radical was prepared and either thiophenol or *p*-methoxythiophenol was slowly added until the color of the radical had nearly disappeared. At that point the solution was shaken with base to remove any excess thiol and then washed three times with water. The toluene solution was dried over magnesium sulfate and the toluene removed on a rotary evaporator. NMR spectra of the crude reaction mixtures showed that the only products were the triarylmethane and the appropriate sulfide. For the reaction with thiophenol, the reaction mixture was chromatographed on a 3 ft × 1 in. alumina column as was done for the reaction of the trityl radical.[27] Elution with petroleum ether followed by 2:1 petroleum ether–benzene did not give complete separation of the triarylmethane and the triarylmethyl phenyl sulfide but the first and last fractions were essentially pure triarylmethane and sulfide, respectively. The products of the reaction with *p*-methoxythiophenol were separated by development of a preparative TLC plate with 2:1 petroleum ether–benzene. NMR spectra and mixture melting points showed the top fraction to be the triarylmethane, and the lower fraction was the tris-*p*-*tert*-butylphenylmethyl *p*-methoxyphenyl sulfide.

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References and Notes

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