Light-catalysed Reduction of Tris(trimethylsilyl)methyl Iodide by Alcohols. A Radical-chain Process showing a Large Kinetic Hydrogen Isotope Effect

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The substituted-alkyl iodide $(Me_3Si)_3CI$ (TsiI) reacted with MeOH in the presence of AgO_3SCF_3, NaOMe, or (less readily) NaOAc under ordinary laboratory light to give $(Me_3Si)_3CH$ (TsiH). Such reduction also took place readily in the presence of the corresponding alkoxide in EtOH or Pr^iOH (in which a second organosilicon product was formed) and markedly less readily in Bu^tOH (in which the second product dominated). In the presence of AgO_3SCF_3, under conditions in which MeOH and EtOH react readily, reaction was markedly slower with Pr^iOH and did not take place with Bu^tOH, Bu^tCH_2OH or $PhCH_2OH$, and the (slow) reaction with CF_3CH_2OH gave a different product. The reaction in MeOH in the presence of AgO_3SCF_3, NaOMe, or NaOAc was inhibited by CCl_4, PhMe or $PhCH_2OH$. In CH_3OD in the presence of NaOMe or AgO_3SCF_3 only undeuteriated TsiH was formed, and in CD_3OD the reaction was very slow. Reactions in CD_3OD–CH_3OD mixtures showed that the kinetic isotope effect for this hydrogen atom abstraction was *ca.* 19 with NaOMe and *ca.* 22 with AgO_3SCF_3 present. The reactions with MeOH appear to involve a radical chain process in which $Tsi^•$ and $I^•$ are formed by homolytic cleavage of the Tsi–I bond, with the $Tsi^•$ radicals then abstracting H atoms from the CH_3 group of CH_3OH to give $^•CH_2OH$ radicals, which abstract $I^•$ from TsiI to regenerate the $Tsi^•$ radicals. It is suggested that the function of NaOMe and AgO_3CF_3 is to remove I_2, which otherwise acts as an effective radical trap.

The effects of the very bulky group $(Me_3Si)_3C$ as a ligand in organometallic compounds have been much studied in recent years but little attention has been paid to the organic chemistry of simple derivatives of the type $(Me_3Si)_3CX$; for example, those with X = halogen. We expected that such compounds would show unusual behaviour under conditions in which ordinary alkyl iodides undergo nucleophilic substitution or elimination, since (*a*) there should be severe steric inhibition of attack of the S_N2 type at the central carbon, and (*b*) formation of the cation $(Me_3Si)_3C^+$ would be strongly disfavoured since an α-Me_3Si is known to have a smaller stabilizing effect than an α-Me group on a carbonium ion, and is probably even destabilizing relative to hydrogen.[1,2] Furthermore, since there are no β-H atoms, β-elimination of the E_1 or E_2 type is impossible. We thus decided to examine the behaviour of the halides $(Me_3Si)_3CX$ towards sodium methoxide or silver salts in methanol, conditions that normally promote nucleophilic substitution at carbon, and the surprising outcome is described below. (A preliminary account of part of the work has appeared.[3])

For convenience, the $(Me_3Si)_3C$ group is subsequently denoted by Tsi.

Results and Discussion

Before we realized that the reactions were initiated by light (see later), experiments were conducted in the open laboratory mainly under artificial lighting. However there was some daylight from fairly distant windows and this must have been somewhat variable, and so only large differences in rates could be regarded as significant. The results left no doubt, however, about the main features of the reaction as set out below, and later some key experiments were conducted under controlled lighting.

The halides TsiCl and TsiBr showed no reaction on prolonged refluxing in MeOH alone, but TsiI did react slowly, *ca.* 7% disappearing in 1 h, and giving rise unexpectedly to the reduction product TsiH. In the presence of 0.10 mol dm^{-3} NaOMe, however, whereas TsiCl and TsiBr remained inert, TsiI (0.020 mol dm^{-3}) reacted fairly rapidly, *ca.* 98% of it disappearing in 1 h under reflux to give TsiH as the sole significant product. Reaction was also *ca.* 98% complete after 1 h in MeOH containing 0.025 mol dm^{-3} AgO_3SCF_3 (subsequently denoted by AgOTf), and again TsiH was the sole detectable product.

To examine the scope of the reaction several other alcohols were used. A solution (0.02 mol dm^{-3}) of TsiI in the alcohol containing either an 0.10 mol dm^{-3} concentration of the corresponding alkoxide or 0.025 mol dm^{-3} AgOTf was boiled under reflux for 1 h. In this time, whereas the reaction with NaOMe–MeOH was essentially complete, that in NaOEt–EtOH was only about half-complete, TsiH being the sole product in each case. In $NaOPr^i$–Pr^iOH the reaction was again *ca.* half-complete, but the product was a 2:1 mixture of TsiH with another Tsi-derivative showing a ^1H resonance at δ 0.18. In $KOBu^t$–Bu^tOH reaction was *ca.* one-third complete, and products appeared to be the same as those formed from Pr^iOH, but in a *ca.* 1:2 ratio. In $NaOCH_2CF_3$–CF_3CH_2OH reaction was very slow, but after 8 h under reflux *ca.* 4% of TsiH had been formed.

When 0.10 mol cm^{-3} NaOAc was used in place of the sodium alkoxide, reaction to give TsiH occurred in refluxing MeOH, EtOH and Pr^iOH, but not in Bu^tOH. However, the rates were markedly lower than in the presence of the alkoxides, substantial amounts of unchanged TsiI remaining after 1 h of refluxing. The unidentified compound formed in $NaOPr^i$–Pr^iOH was not observed, suggesting that strong base is needed for its formation.

The reactions with refluxing MeOH, EtOH and Pr^iOH in the presence of AgOTf all went essentially to completion within 1 h, and TsiH was the only detectable product. Reaction with AgOTf–CF_3CH_2OH went only to *ca.* 12% completion in 1 h; only about 2% of TsiH was formed, and the major product had a ^1H NMR spectrum suggesting that it was of the type $(Me_3Si)_2C(Me)SiMe_2X$. Such a product could be expected if the cation $(Me_3Si)_3C^+$ were actually or incipiently formed, since migrations of Me groups from silicon to adjacent electron-deficient carbon are well known; *e.g.* in the reaction of Me_3SiCH_2Cl with $AlCl_3$.

To obtain more detailed information about the relative reactivities of various alcohols in the reaction catalysed by AgOTf, 1.0 mol dm^{-3} solutions of the alcohols ROH in benzene containing 0.020 mol dm^{-3} AgOTf were kept at *ca.* 82 °C for 1 h. Under these conditions *ca.* 25–30% of the TsiI reacted with MeOH or EtOH, to give TsiH, but there was only *ca.* 5% reaction with Pr^{i}OH, and none with Bu^{t}OH, Bu^{t}CH$_2$OH or PhCH$_2$OH. When the neat alcohols containing 0.02 mol dm^{-3} AgOTf were used, *ca.* 85% reaction took place in 1 h at 82 °C in the case of Pr^{i}OH, but there was no detectable reaction in the case of Bu^{t}OH, Me$_3$CCH$_2$OH or PhCH$_2$OH. However, in 4 h all of the last three alcohols gave small amounts ($< 5\%$) of TsiH.

A very revealing observation was that when 1.0 mol dm^{-3} CD$_3$OD in benzene containing 0.020 mol dm^{-3} AgOTf was used there was no detectable reaction after 1 h at 82 °C. This indicated not only that the rate-determining step must involve hydrogen-transfer from the alcohol but also that a large kinetic isotope was involved. When reaction was carried out with 0.020 mol dm^{-3} TsiI in refluxing CH$_3$OD containing either 0.10 mol dm^{-3} NaOCH$_3$ or 0.20 mol dm^{-3} AgOTf only undeuteriated TsiH was formed, showing that the hydrogen transfer was from a C–H rather than the O–H bond. When 1:1 CD$_3$OD–CH$_3$OD was used the TsiH:TsiD product ratio was *ca.* 95:5, corresponding to a kinetic isotope effect of roughly 20, in both the base and silver salt catalysed reactions. For more accurate determination of the kinetic isotope effect, in the base-catalysed reaction a 7.9:1 CD$_3$OD–CH$_3$OD mixture was used, and this resulted in deuterium incorporation of 29.5%. For the silver salt catalysed reaction in 9.2:1 CD$_3$OD–CH$_3$OD the deuterium incorporation was 29.4%. These values correspond to kinetic isotope effects of *ca.* 19 and 22, respectively, probably not significantly different. Values of comparable magnitude have frequently been observed for proton or hydrogen atom transfers to very sterically hindered bases or radicals, respectively, and are normally attributed to quantum mechanical tunnelling.[4]

That the reactions involved C–H and not O–H bond in the rate-determining step pointed to the participation of the free radical Tsi$^{\bullet}$. This radical is known to be highly persistent,[5,6] and it would be expected to abstract H rather than D from CH$_3$OD. (The radical Me$^{\bullet}$ has been shown to abstract a hydrogen atom from the carbon of MeOH rather than from the oxygen.[7]) To confirm that the Tsi$^{\bullet}$ radical would react in this way, it was generated by UV photolysis of Tsi$_2$Hg (*cf.* ref. 5) in a 1:1 CD$_3$OD–CH$_3$OD mixture containing 10 vol% of CCl$_4$, the presence of which was necessary to bring the mercurial into solution. The product mixture contained rather more than 50% of TsiCl, formed by abstraction of Cl$^{\bullet}$ from CCl$_4$, but the TsiH:TsiD ratio of *ca.* 96:4, was sufficiently close to that in the TsiI reactions to support the view that Tsi$^{\bullet}$ radicals are involved in all cases.

Up to this point it had appeared that the reaction with MeOH was initiated by NaOMe or AgOTf and thus that these were responsible for the generation of Tsi$^{\bullet}$ radicals, but we could think of no realistic way in which they could act in this manner. We thus had to consider the possibility that light was responsible for the initiation, though this seemed unlikely since the reduction reactions described above all took place in glass vessels in ordinary laboratory light and TsiI does not absorb in the visible region sufficiently to be coloured. We found that, in fact, the iodide has λ_{max}(EtOH) at a distinctly higher wave length (293 nm) than do common alkyl iodides (*cf.* λ_{max} 259 nm for MeI) and that the absorption extends well into the visible, the value of ε at 340 nm being *ca.* 10% of that (*ca.* 475 nm) at λ_{max}, and still significant at 360 nm. That light was, indeed, responsible for initiation of the reaction was confirmed by the observation that when it was excluded no reaction took place in refluxing MeOH containing either NaOMe or AgOTf, and that when a quartz vessel exposed to UV light was used the reactions were very fast even at room temperature. It was thus clear that the function of NaOMe and AgOTf was to assist a light-induced reaction, and the most likely way was by interfering with a chain-terminating step in a radical-chain process. It is appropriate at this stage to consider what steps this process might involve.

A possible sequence for the reaction in the presence of AgOTf is shown in Scheme 1. In this sequence, after the light-induced generation of Tsi$^{\bullet}$ and I$^{\bullet}$ the Tsi$^{\bullet}$ radical abstracts an H atom from CH$_3$OH to give the radical $^{\bullet}$CH$_2$OH [eqn. (*b*)] which then abstracts $^{\bullet}$I from TsiI to regenerate Tsi$^{\bullet}$ [eqn. (*c*)]. Likely chain-terminating processes are: (i) combination of Tsi$^{\bullet}$ radicals and I$^{\bullet}$ atoms to regenerate TsiI [eqn. (*d*)]; (ii) combination of Tsi$^{\bullet}$ and $^{\bullet}$CH$_2$OH to give TsiCH$_2$OH [eqn. (*f*)] (which was not detected); (iii) combination of I$^{\bullet}$ and $^{\bullet}$CH$_2$OH to give ICH$_2$OH {which would break down to give HCHO and HI [eqn. (*k*)]}; (iv) removal of Tsi$^{\bullet}$ by reaction with I$_2$ {formed by dimerization of I$^{\bullet}$ [eqn. (*e*)]}; and (v) removal of $^{\bullet}$CH$_2$OH by dimerization [eqn. (*j*)] or by reaction with I$_2$ [eqn. (*i*)]. Dimerization of Tsi$^{\bullet}$ radicals to give (Me$_3$Si)$_3$CC(SiMe$_3$)$_3$, in principle a possible chain-terminating process, is sterically inhibited.[5,6]

$$\mathrm{TsiI} \xrightarrow{h\nu} \mathrm{Tsi}^{\bullet} + \mathrm{I}^{\bullet} \tag{a}$$

$$\mathrm{Tsi}^{\bullet} + \mathrm{CH_3OH} \longrightarrow {}^{\bullet}\mathrm{CH_2OH} + \mathrm{TsiH} \tag{b}$$

$$\mathrm{TsiI} + {}^{\bullet}\mathrm{CH_2OH} \longrightarrow \mathrm{Tsi}^{\bullet} + \mathrm{ICH_2OH} \tag{c}$$

$$\mathrm{Tsi}^{\bullet} + \mathrm{I}^{\bullet} \longrightarrow \mathrm{TsiI} \tag{d}$$

$$\mathrm{I}^{\bullet} + \mathrm{I}^{\bullet} \longrightarrow \mathrm{I_2} \tag{e}$$

$$\mathrm{Tsi}^{\bullet} + {}^{\bullet}\mathrm{CH_2OH} \longrightarrow \mathrm{TsiCH_2OH} \tag{f}$$

$$\mathrm{I}^{\bullet} + {}^{\bullet}\mathrm{CH_2OH} \longrightarrow \mathrm{ICH_2OH} \tag{g}$$

$$\mathrm{Tsi}^{\bullet} + \mathrm{I_2} \longrightarrow \mathrm{TsiI} + \mathrm{I}^{\bullet} \tag{h}$$

$${}^{\bullet}\mathrm{CH_2OH} + \mathrm{I_2} \longrightarrow \mathrm{ICH_2OH} + \mathrm{I}^{\bullet} \tag{i}$$

$$2{}^{\bullet}\mathrm{CH_2OH} \longrightarrow \mathrm{(HOCH_2)_2} \tag{j}$$

$$\mathrm{ICH_2OH} \longrightarrow \mathrm{HCHO} + \mathrm{HI} \tag{k}$$

Scheme 1 Suggested course of the reduction of TsiI to TsiH by MeOH under laboratory lighting

The function of AgOTf appears to be to eliminate I$_2$ (and perhaps to inhibit its formation by removing HI from the system), which otherwise acts as a very effective chain-breaker [eqns. (*h*) and (*i*)].

In the presence of NaOMe alternative chain-propagating steps arise because the $^{\bullet}$CH$_2$OH radical would be expected to be rapidly deprotonated by MeO$^-$ since $^{\bullet}$CH$_2$OH is reported to have a pK_a of 10.7,[8] and so reaction (*c*) would be replaced by (*c*′) below, and reactions (*f*), (*g*), (*i*), (*j*) and (*k*) by the corresponding processes with $^{\bullet}$CH$_2$O$^-$ in place of $^{\bullet}$CH$_2$OH.

$$\mathrm{TsiI} + {}^{\bullet}\mathrm{CH_2O^-} \longrightarrow \mathrm{Tsi}^{\bullet} + \mathrm{ICH_2O^-} \quad (\longrightarrow \mathrm{HCHO} + \mathrm{I^-}) \tag{c'}$$

Since dimerization of $^{\bullet}$CH$_2$O$^-$ radicals [in the step corresponding to (*j*)] would involve combination of two negatively-charged species and so be relatively slow, part of the effect of NaOMe could possibly be attributed to this change in a chain-terminating process. The base probably mainly functions, however, by removing I$_2$ to give MeOI [eqn. (*l*)] (which then

$$\mathrm{MeO^-} + \mathrm{I_2} \longrightarrow \mathrm{I^-} + \mathrm{MeOI} \tag{l}$$

Table 1 Effect of added inhibitors on the rate of reduction of 0.015 mol dm^{-3} TsiI in 0.1 mol dm^{-3} NaOAc–MeOH at 65 °C

	Reaction[a] (%)							
t/h	None	CCl_4 (0.25)[b]	CCl_4 (0.5)	PhMe (0.25)	PhMe (0.50)	PhMe (2.0)	$PhCH_2OH$ (0.25)	$PhCH_2OH$ (0.5)
0.5	70	5	4	11	6	3	5	4
1.0	90	13	4	17	10	4	9	5
2.0	98	23	11	25	17	8	10	6
6.0	—	52	11	50	44	14	13	10

[a] With toluene or benzyl alcohol present, the only observed product was TsiH. In the presence of CCl_4, TsiCl was also formed. [b] Inhibitor concentrations in mol dm^{-3}.

decomposes[9]), and by neutralizing formed HI which might otherwise generate further I_2. The poorer nucleophile and weaker base NaOAc would be much less effective in reducing the I_2 content.

In terms of the proposed reaction sequence, no great difference would be expected between the rates in MeOH, EtOH and Pr^{i}OH, since the reduction in the number of available α-hydrogens will be countered by the increasing ease of forming a secondary and a tertiary rather than a primary alkyl radical. In the case of Bu^{t}OH, however, there are no α-Hs available and so any reaction is very slow. With $PhCH_2OH$ the Ph(HO)HC$^{\bullet}$ radical is probably too unreactive to abstract I$^{\bullet}$ from TsiI, and in Me_3CCH_2OH, although there are α-Hs available, approach to them by the very bulky Tsi$^{\bullet}$ radical would be severely sterically inhibited. The low reactivity of CF_3CH_2OH can be attributed to the inhibitory polar effect of the CF_3 group on the ease of abstraction of an adjacent hydrogen, as observed for the reaction of this alcohol with the radical Bu^{t}O$^{\bullet}$.[10] If the reaction sequence is that shown, then other radical traps should inhibit reaction even when NaOMe, NaOAc or AgOTf is present to remove iodine, wholly or partly. In order to see whether this was the case we carried out the reaction with refluxing MeOH in the presence of NaOAc and either CCl_4, PhMe or $PhCH_2OH$, with the results shown in Table 1. All three additives markedly lowered the rate, $PhCH_2OH$ and CCl_4 being distinctly more effective than PhMe. In the case of CCl_4, TsiCl was also formed, at roughly the same rate as TsiH, with 0.5 mol dm^{-3} CCl_4 and at about one-third that rate with 0.25 mol dm^{-3} CCl_4. The reactions in the presence of NaOMe or AgOTf were also clearly slower in the presence of the additives but no attempt was made to determine the extent of the inhibition.

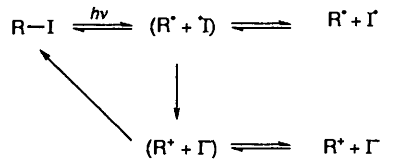
Another implication of the proposal that the function of the base (as of AgOTf) is to remove iodine is that once sufficient base is present to neutralize all the HI formed and leave a small excess to remove I_2, increase in the base concentration should have little further effect. Under subdued lighting, in a darkened room with illumination from two 65 W fluorescent tubes 3 m from the glass vessel, the reaction in the presence of NaOMe was slow enough to allow rough measurement of the rate. It was found that there was always an induction period, which varied from run to run in the range 5–15 min. After the induction period approximate first-order plots were obtained, giving rate constants reproducible to within ±20%. The results showed that the rate of reduction was independent of the concentration of NaOMe in the range 0.05–0.20 mol dm^{-3}, and also that the rate with 0.10 or 0.20 mol dm^{-3} NaOMe present was *ca.* 10 times that at the same concentrations of NaOAc. In keeping with the reasons suggested earlier for the greater rate enhancement by NaOMe than by NaOAc, when the reactions with 0.10 mol dm^{-3} NaOMe or NaOAc were carried out in the presence of 0.001 mol dm^{-3} I_2 the reaction went rapidly to completion in the case of NaOMe but was completely inhibited in that of NaOAc.

The reactions with AgOTf (0.020 mol dm^{-3}) did not yield first-order plots, and the rates varied substantially from run to run, not surprisingly since AgI separates during the reaction and interferes with access of light to the TsI. However, the median length of the induction period and median half-life were roughly the same as those in the presence of NaOMe, which is what would be expected if both the base and silver salt remove essentially all of the iodine.

The induction period may be partly due to the time taken to build up stationary concentrations of Tsi$^{\bullet}$ and $^{\bullet}CH_2OH$ (or $^{\bullet}CH_2O^-$) radicals but is probably mainly attributable to the presence of traces of an inhibitor (perhaps oxygen) that must be used up before the chain process can operate. In keeping with this, when fresh TsiI was added to solutions (containing NaOMe) in which a reaction had already gone to completion the induction periods were all in the 5 min region, but we cannot be sure that this was statistically significant.

We believe that our observations leave no doubt that the reduction of TsiI to TsiH in MeOH involves initial photolysis to give Tsi$^{\bullet}$ radicals and that a rate-limiting step involves abstraction of H atoms from the C–H bonds of CH_3OH by these radicals. We think that we have also identified the other main features of the mechanism, and in particular that AgOTf and NaOMe promote the reaction mainly or wholly by removing I_2, which otherwise acts as an effective radical trap. Detailed kinetic studies under very carefully controlled illumination would be necessary to elucidate all the aspects unambiguously.

Extensive studies by Kropp and his co-workers have shown that reactions of alkyl and other organic iodides with MeOH are promoted by UV irradiation and that both cationic and radical intermediates are involved.[11,12] The formation of cations, thought to be produced by electron transfer within the initial radical pair inside a solvent cage, as represented in Scheme 2, is normally favoured. Such reactions have not, as far as we are aware, been examined in the presence of NaOMe or silver salts, which in our reaction promote the radical process, but in some systems studied by Kropp *et al.* the presence of Et_3N led to a higher yield of radical-derived products.[2] (In those systems the presence of zinc powder to remove iodine led to an increase in rate but did not affect the product balance.) The special features of the reaction of TsiI with MeOH are that (i) the reaction is induced by low energy light passing through Pyrex glassware, (ii) cationic intermediates play no significant part, and (iii) little reaction takes place in the absence of base or



Scheme 2

a silver salt. These features can perhaps be partly accounted for as follows. (i) The homolytic cleavage of the Tsi–I bond is facilitated by stabilization of the radical centre arising from electronic effects of the α-Me_3Si groups[13] and by relief of steric strain. Recombination of $Tsi^{\bullet}$ and $I^{\bullet}$ will be correspondingly inhibited, which is important since recombination of $R^{\bullet}$ and $I^{\bullet}$ formed by irradiation of ordinary alkyl iodides is normally an efficient process.[14] (ii) The carbocation Tsi^+ is destabilized by its α-Me_3Si groups. (iii) The inhibitory effect of iodine in the radical process could have been overlooked by Kropp *et al.* because their attention was focused on the cation route, which predominated in their systems; moreover the cation route does not produce I_2 (but instead I^-, which would take up some I_2 as I_3^-). Furthermore the effect of absorption of light by the I_2 may be less important for UV light.

Experimental

Tris(trimethylsilyl)methyl Iodide.—This was prepared by the reaction of TsiLi with I_2, as described previously,[15] and was recrystallized from ethanol. It contained 15% of TsiMe, and no attempt was made to remove this because it is inert towards all the reagents used and provided a very useful internal standard for determination of yields by ^1H NMR spectroscopy. The bulk sample was always protected from light, and when not used was stored at −20 °C.

General Procedures.—All reactions were carried out under argon. Unless otherwise specified, experiments were conducted under artificial light in roughly the same position in the open laboratory, well away from windows. Because of the inevitable variability of the intensity of light reaching the reaction mixture only large rate differences are significant; comparison of results obtained within a given set of experiments at one time (for example, those with NaOR–ROH for various R) is more reliable than that between results for a different set (*e.g.* between those with NaOR–ROH and those with AgOTf–ROH).

Products were identified by comparison of their ^1H and ^{13}C NMR spectra with those of authentic samples. Yields were determined from the integrated signals from the Me_3Si protons of the Tsi groups of TsiI, TsiH, TsiCl and TsiMe, which appeared at δ 0.27, 0.10, 0.19 and 0.07, respectively. The ^1H NMR spectroscopic analyses were performed with a Varian Unity 300 spectrometer equipped with a switchable probe operated at 75.426 MHz. For spectra determined in $CDCl_3$ the residual $CHCl_3$ peak was used as reference. When products were extracted into CCl_4 for analysis a small amount of $CDCl_3$ was added as lock and internal reference.

Reactions with NaOR–ROH.—A solution of TsiI (35 mg, 0.10 mmol) in NaOR–ROH (0.1 mol dm^{-3}; 5 cm^3) was refluxed for 1 h. The solution was then cooled and added to a mixture of CCl_4 (2 cm^3) and hydrochloric acid (0.1 mol dm^{-3}; 10 cm^3) in a separating funnel. The organic layer was separated and dried over a little anhydrous Na_2SO_4. Some (*ca.* 0.5 cm^3) $CDCl_3$ was added and the ^1H NMR spectrum recorded. The results were as follows.

R = Me. Reaction was *ca.* 98% complete. The only significant product was TsiH. When the reaction was repeated with MeOH alone, there was *ca.* 7% conversion into TsiH.

R = Et. Reaction was *ca.* 60% complete; TsiH was formed in *ca.* 36% yield, and there were traces of other products.

R = Pr^i. Reaction was *ca.* 35% complete. TsiH was formed in 20% yield and there was another product (δ 0.18) in *ca.* 11% yield.

R = Bu^t. Reaction was *ca.* 30% complete. The main product (20%) was the unidentified species found in the preceeding reaction, and TsiH was formed in *ca.* 8% yield.

R = CF_3CH_2OH. There was no detectable reaction. However, when $NaOCH_2CF_3$ (0.20 mol dm^{-3}) was used, after 8 h *ca.* 4% of TsiH had been formed.

Reactions in NaOAc–ROH.—The procedure was as described above but with NaOAc in place of NaOMe. Sufficient of this was present to give a 0.10 mol dm^{-3} solution, but only in MeOH and EtOH did it dissolve completely even under reflux. Some TsiH was formed in each alcohol except Bu^{t}OH, but much less than in NaOMe–MeOH. The rates in MeOH, EtOH and Pr^{i}OH (at their boiling points) were roughly in 4:2:1 ratio.

Reactions with AgOTf–ROH.—The procedure was as described above but with AgOTf (0.025 mol dm^{-3}) in ROH. The results were as follows.

R = Me, Et or Pr^i. Reactions were > 98% complete. The sole product was TsiH in each case.

Bu^{t}OH. There was no detectable reaction. (Later when a higher light level was used a little TsiH was formed on prolonged refluxing.)

R = CF_3CH_2OH. Reaction was *ca.* 12% complete. Less than 2% of TsiH was formed, and the major products gave peaks in the ^1H NMR spectrum at δ 0.08, 0.18 and 1.11, in a *ca.* 6:2:1 integration ratio.

Reactions in the Presence of Inhibitors.—Reaction with MeOH containing NaOMe or NaOAc (0.10 mol dm^{-3}) or AgOTf (0.025 mol dm^{-3}) were performed in the way described above but were allowed to proceed for varying periods. Small aliquots were removed from time to time and the organic products extracted into CCl_4 as before. In the absence of inhibitor the reactions in the presence of NaOMe (0.10 mol dm^{-3}) or AgOTf (0.025 mol dm^{-3}) had half-lives of only a few minutes, whereas with NaOAc (0.10 mol dm^{-3}) the half-life was *ca.* 30 min. Details are as follows.

NaOMe–MeOH *containing* CCl_4 (1.0 mol dm^{-3}). The reaction was allowed to proceed for 3 h, with samples withdrawn at 1 h intervals. Less than 6% of reaction took place. The products were TsiCl and TsiH; the relative yields of these were difficult to assess because of the small amounts present, but the TsiCl peak appeared to be slightly greater in area than the TsiH peak.

AgOTf–MeOH *containing* CCl_4 (1.0 mol dm^{-3}). The procedure was carried out as above. The reaction was faster and was *ca.* 18% complete in 3 h. The products were again TsiCl and TsiH, in roughly 2:1 ratio.

NaOAc–MeOH *containing* CCl_4, PhMe *or* $PhCH_2OH$ (1.0 mol dm^{-3}). The procedure was as above but the reaction was carried on for 6 h, and samples were withdrawn after 0.5, 1.0, 2.0 and 6.0 h. The results are summarized in Table 1.

Reaction with NaOMe–MeOH *or* NaOAc–MeOH *in the presence of* I_2. The presence of I_2 (0.001 mol dm^{-3}) had no effect on the rate in NaOMe–MeOH but completely inhibited the reaction in NaOAc–MeOH.

Reactions with ROH (1.0 mol dm^{-3}) *in Benzene containing* AgOTf (0.023 mol dm^{-3}).—Sufficient ROH was introduced from a microsyringe into a solution of AgOTf (0.023 mol dm^{-3}) in benzene (5 cm^3) to give a 1.0 mol dm^{-3} concentration of the alcohol. The vessel (fitted with a short air condenser) was immersed in the vapour from refluxing Pr^{i}OH (b.p. 82 °C) and after *ca.* 10 min TsiI (*ca.* 35 mg, 0.10 mmol) was added. After 1 h the solution was added to water and the organic layer was separated, washed, and dried (Na_2SO_4) and most of the solvent was carefully evaporated off at room temperature under reduced pressure. The residue was taken up in $CDCl_3$ and the ^1H NMR spectrum was determined. Results were as follows.

R = Me *or* Et. The reactions were respectively *ca.* 25 and

32% complete (the difference is not significant). Only TsiH was formed.

R = Pr^i. Reaction was only 5% complete and TsiH was the only detectable product. When neat Pr^{i}OH was used under otherwise identical conditions *ca.* 85% of **1** was converted into TsiH.

R = Bu^{t}OH, Bu^{t}CH$_2$OH *or* PhCH$_2$OH. There was no detectable reaction. When the neat alcohols were used under otherwise identical conditions no detectable reaction took place in 1 h, but after 4 h a little TsiH (< 5%) was present in each case.

Reactions Under Controlled Lighting.—In order to gain better information on the rates of reaction with MeOH a series of experiments was carried out in the one set of apparatus in a darkened room with light only from two 65 W fluorescent tubes situated *ca.* 3 m from the reaction vessel. Reactions were carried out and monitored as described above for reactions in the presence of inhibitors.

Reactions in NaOMe–MeOH. The solution contained TsiI (0.005 mol dm^{-3}) and NaOMe (0.05–0.20 mol dm^{-3}). Induction periods of 5–15 min were observed, the period showing no discernible pattern with respect to the concentration of TsiI or NaOMe. After the induction period approximate first-order plots were obtained, and rate constants were reproducible to within *ca.* ± 20%. Within these limits the half-life (mean value 14 min) was the same for initial concentrations of **1** of 0.0050 and 0.01 mol dm^{-3}. Several runs were carried out by adding a further sample of **1** to solutions in which reactions had been carried essentially to completion; in each there was again an induction period, but at the low end (*ca.* 5 min) of the usual range.

Reaction in NaOAc–MeOH. Both 0.10 and 0.20 mol dm^3 solutions of NaOAc were used. The induction periods were consistently at the low end of the range observed with NaOMe and the rate constant was roughly one-tenth of that with NaOMe present.

Reactions with AgOTf *in* MeOH. Reactions were carried out with AgOTf in the range 0.005–0.05 mol dm^{-3}. Reproducibility was poor and first-order plots were not linear. Induction periods were in the range observed with NaOMe. Increasing the concentration of AgOTf seemed, if anything, to reduce the rate somewhat.

Kinetic Isotope Effects.—Reactions of TsiI (0.02 mol dm^{-3}) were carried out for 1 h under reflux in CH$_3$OH–CD$_3$OH mixtures containing sodium methoxide (0.10 mol dm^{-3}) or AgOTf (0.025 mol dm^{-3}). The product was extracted into CCl$_4$ as usual, the ^{1}H NMR spectrum was recorded to check the identity of the products, and the solution was then examined by GLC-MS by use of a Kratos Model MS-80RFA mass spectrometer. With 1:1 CH$_3$OH–CD$_3$OD mixtures in the presence of either NaOMe or AgOTf the TsiH:TsiD ratio was *ca.* 95:5, corresponding to a kinetic isotope effect of roughly 20. With CH$_3$OD only TsiH was formed. In 7.9:1 CD$_3$OD:CH$_3$OH containing NaOMe the TsiH:TsiD ratio was 2.93, and in 9.2:1 CD$_3$OD–CH$_3$OH containing AgOTf it was 3.01, the ratios corresponding to kinetic isotope effects of 19 and 22, respectively.

For determination of the kinetic isotope effect for radicals generated from Tsi$_2$Hg the latter (*ca.* 0.02 mol dm^{-3}) was dissolved in 1:1 CH$_3$OD–CD$_3$OD containing 10 vol% of CCl$_4$ to bring the mercurial into solution. The mixture, in a quartz vessel, was irradiated in a Rayonet Photochemical Reactor with light of 2537 Å wavelength from a low pressure mercury lamp. Somewhat more than 50% of the product was TsiCl, but this did not interfere with determination of the TsiH:TsiD ratio, which was *ca.* 96:4.

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