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REACTIONS OF SOME STERICALLY-HINDERED ORGANOSILICON HYDRIDES AND IODIDES WITH HALOGENS

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Summary

The reaction of $TsiSiMe_2H$ (I) ($Tsi = (Me_3Si)_3C$) with I_2 or with a molar equivalent of ICl gives the iodide $TsiSiMe_2I$ (II) in hydroxylic media (MeOH, CH_3CO_2H, CF_3CO_2H) as it does in CCl_4. The reaction with I_2 is very fast in CF_3CO_2H, but in MeOH is only about as fast as in CCl_4. The iodide II reacts with ICl in MeOH to give a mixture of $TsiSiMe_2OMe$ (III) and $TsiSiMe_2Cl$ (IV), but the reaction is markedly slower than that in CCl_4 (in which IV is formed). The hydride I also reacts with INO_3 in MeOH to give II, and the latter reacts with INO_3 to give III. The reactions of $TsiSiPh_2H$ (V) and $TsiSiPh_2I$ (VI) with ICl in MeOH are markedly slower than those of I and II; even with one equivalent of ICl in MeOH, V gives a mixture of VI and the (rearranged) methoxide $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$ (VII). Reaction of VI with ICl in MeOH gives VII and the rearranged chloride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$.

The formation of methoxides in the reactions of the iodides II and VI with ICl in MeOH, and the rearrangements observed in the case of VI, are consistent with a mechanism involving an intermediate silicocation. Other mechanistic aspects are discussed.

Introduction

It was observed previously that the highly hindered organosilicon hydrides $TsiSiR_2H$ ($Tsi = (Me_3Si)_3C$ = "trisyl"; R = Me or Ph) react with one molar proportion of ICl in CCl_4 to give the corresponding iodides $TsiSiR_2I$, but with an excess of ICl to give chlorides; for R = Me the chloride obtained was $TsiSiMe_2Cl$, but for R = Ph it was the rearranged species $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$ [1,2]. It was further demonstrated that the iodides $TsiSiR_2I$ react with ICl to give these same chlorides [2]. For the reactions between the hydrides and ICl, a mechanism involving a polar transition state (A), based on proposals by Sommer for the reaction of other silicon hydrides with BrCl [3] was assumed. The reactions between the iodides and

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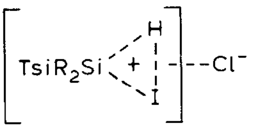
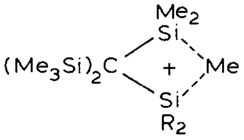
ICl were suggested to proceed through a bridged cation (**B**), as in equations 1a and 1b, the proportions of the two products depending on the nature of R.



(**A**)



(**B**)

$$\mathrm{TsiSiR_2I + ICl \rightleftharpoons (B)[I_2Cl]^-} \qquad (1a)$$

$$\mathrm{(B)[I_2Cl]^- \rightarrow TsiSiR_2Cl + (Me_3Si)_2C(SiR_2Me)(SiMe_2Cl)} \qquad (1b)$$

To throw further light on the mechanisms we decided to examine these and some related reactions in MeOH, since (a) if the reactions of the hydrides with halogens proceed through a polar transition state, such as **A**, they could be expected to take place much more readily in this solvent than in CCl_4 but to give the same products, and (b) if the reactions of the iodides with ICl do involve ionization, as in equations 1a and 1b, the methanol could be expected to trap some of the cations to give silicon methoxide products. A few reactions in some other hydroxylic media, and some with other halogens, have also been examined.

Results and discussion

When a solution of Br_2 (0.35 mmol) in MeOH (3 cm^3) was mixed with a solution of $TsiSiMe_2H$ (I) (0.35 mmol) in MeOH (10 cm^3) at room temperature the colour was immediately discharged. After 10 min the solvent was evaporated off at room temperature under vacuum to leave exclusively the bromide $TsiSiMe_2Br$. (The rate of the second order reaction of I with Br_2 in CCl_4 has previously been shown to be comparable with that for other trialkylsilanes [4].) Similar behaviour was observed with ICl, and the product was exclusively $TsiSiMe_2I$ (II). In a reaction involving I (0.35 mmol) and ICl (0.35 mmol) in MeOH (10 cm^3), examination of the reaction solution after 15 min by ^1H NMR spectroscopy revealed that only the iodide II was present (run 1, in Table 1), whereas reaction with I_2 under rather similar conditions (but with 15 cm^3 of MeOH) gave only 26% of II in 5 h (run 6 in Table 1). Reactions between I (0.35 mmol) and I_2 (0.35 mmol in 8 and 16 cm^3 of MeOH gave ca. 20 and 10%, respectively, of the iodide II after 1 h (runs 10 and 11 in Table 1), suggesting that the reaction is probably approximately first order with respect to the iodine. The absence of any $TsiSiMe_2OMe$ in the products is consistent with a mechanism in MeOH (such as that involving transition state **A**), which does not involve a trappable intermediate. (It is relevant to note that this could not have been demonstrated with ordinary triorganosilanes because the initially formed silicon iodide would be very rapidly converted into the methoxide.)

The reactions of I with halogens in some other solvents were briefly examined. In CH_3CO_2H, I reacted rapidly with Br_2 and with I_2 to give $TsiSiMe_2Br$ and $TsiSiMe_2I$, respectively. Reactions between I (0.35 mmol) and I_2 (0.35 mmol) in various solvents (15 cm^3) for 5 h at room temperature gave 26% of II in MeOH, 26% in CCl_4, 57% in CH_3CO_2H (runs 6–8 in Table 1), and 100% in CF_3CO_2H/CCl_4 (12/3 v/v). (The CF_3CO_2H could not be satisfactorily used on its own because of the poor solubility

TABLE I

REACTIONS OF $TsiSiMe_2H$ (I) AND $TsiSiMe_2I$ (II) WITH HALOGENS, XY.

Run No.	Silane (mmol)	XY (mmol)	Solvent (cm^3)	Temperature (°C)	Time (h)	Product composition (%)
1	I (0.35)	ICl (0.35)	MeOH (10)	21	0.25	II 100
2	I (0.35)	ICl (2.8)	MeOH (13)	21	0.25	II 93; III 7
					5	II 46; III 39; IV 15
					28	II 13; III 66; IV 21
3	II (0.24)	ICl (1.92)	MeOH (13)	21	0.25	II 92; III 8
					24	II 19; III 68; IV 13
4	II (0.24)	ICl (0.24)	CCl_4 (10)	21	0.5	II 77; IV 23
					3	II 46; IV 54
5	II (0.24)	ICl (0.24)	MeOH (10)	21	24	II 100
6	I (0.35)	I_2 (0.35)	MeOH (15)	21	5	I 74; II 26
7	I (0.35	I_2 (0.35)	CCl_4 (15)	21	5	I 74; II 26
8	I (0.35)	I_2 (0.35)	CH_3CO_2H (15)	21	5	I 43; II 57
9	I (0.35	I_2 (0.35)	CF_3CO_2H (12)/CCl_4 (3)	21	0.1	II 100
10	I (0.35)	I_2 (0.35)	MeOH (8)	21	1	I 80; II 20
					6	I 67; II 33
11	I (0.35)	I_2 (0.35)	MeOH (16)	21	1	I 90; II 10
					6	I 76; II 24
12	I (0.035)	I_2 (0.035)	CF_3CO_2H (0.7)/CCl_4 (0.3)	ca. 28 [a]	0.033 [b]	I 28; II 72
					0.1	II 100
13	II (0.24)	I_2 (1.92)	MeOH (10)	ca. 60	24	II 25; III 75

[a] See Experimental section. [b] 2 min; see Experimental section.

of iodine in it.) The reaction in CF_3CO_2H/CCl_4 was examined in an NMR tube (at a temperature between that of the room, ca. 21°C, and that of the probe, 35°C) (run 12 in Table 1), and found to be 72% complete after approximately 2 min; the solution was colourless when the tube was removed from the probe, and when it was returned to it after a total reaction time of about 6 min, reaction was complete (run 7 in Table 1). The high rates in CF_3CO_2H are consistent with observations on reactions of halogens with olefins or aromatics [5,6]. The close similarity of the rates in MeOH and CCl_4 may be misleading, since the reactions in CCl_4 are likely to be of high order in the halogen [7] and comparisons at other concentrations might give markedly different results. It is clear, however, that with these two solvents the picture is very different, for example, from that for additions of bromine to olefins, in which the second order rate constants are some 10^6–10^7 times as large in MeOH as in CCl_4 [8]. The comparability of the rates of iodination of I in MeOH and CCl_4 would suggest that there is little charge development in the transition state, and is especially surprising in view of the observation that the reaction of triorganosilanes with Br_2 is much faster in CCl_4 than in n-octane and the conclusion that this is due to the difference in the polarities of the two media [4]. The situation seems closer to that in, for example, cleavage of R–Sn bonds of R_4Sn species by halogens; e.g., the second order rate constants for the reaction of Bu_4Sn with Br_2 are almost the same in CH_3CO_2H as in CCl_4 [9]. These cleavages are thought to involve cyclic four-centre transition states with little charge separation, and development of little charge in the transition state for the halogenation of silicon hydrides would be consistent with the observation that reaction of $PhMe_2SiH$ with Br_2 shows a very small isotope effect, viz. 1.24 ± 0.15, suggesting that Si–H bond breaking has preceded to only a very small extent in the transition state [10] (although this value would in itself be equally consistent with a very large degree of Si–H bond breaking compensated by a large degree of H–Br bond making). On the other hand, the effects of varying the substituents in the organic group of triorganosilanes [3,4,7,11] (for example, in the reaction of $XC_6H_4SiMe_2H$ species with Br_2 in CCl_4 [4]) indicate that a significant amount of positive charge is developed on the silicon atom in the transition state. It could be argued that the systems we have studied are atypical, in that solvation, especially nucleophilic solvation of the partly positively charged silicon centre, may be sterically inhibited, but the fairly normal reactivity of $TsiSiMe_2H$ in the reaction with Br_2 in CCl_4, in which (in the light of the substantially higher rates in CCl_4 than in n-octane) solvation is thought to be important [4], argues against this.

The effectiveness of solvent CF_3CO_2H in facilitating the iodination probably originates in rather specific interaction between the acidic hydrogen and the forming I^- centre [5], perhaps even involving a preassociation of the I_2 and the acid.

In our view the mechanism represented by transition state (A) [3] does not provide a wholly satisfactory interpretation of all the available results on the interaction between silicon hydrides and halogens, but no better suggestion has been made.

$TsiSiMe_2H$ (I)

$TsiSiMe_2OMe$ (III)

$TsiSiMe_2I$ (II)

$TsiSiMe_2Cl$ (IV)

When the hydride I (0.35 mmol) was treated with 8 molar equivalents of ICl in MeOH (13 cm^3) (run 2 in Table 1), after 15 min at room temperature the iodide II and the methoxide III were present in 93/7 ratio; after 5 h these species and the chloride IV were present in 46/39/15 ratio, and after 28 h the corresponding ratio was 13/66/21. When the iodide II was taken with 8 equivalents of ICl in MeOH (run 3 in Table 1), II and III were present in 92/8 ratio after 15 min, and II, III, and IV in 19/68/13 ratio after 24 h. The higher III/IV ratio observed in the reaction of II compared with that in the reaction starting from I may not be real, but some difference would not be surprising since an equivalent of HCl or HI (or a mixture of both) is present during the reaction of II generated in situ from I. It should be emphasized that none of the methoxide, III, is formed by solvolysis of the chloride IV; the latter was recovered unchanged when a solution of it (0.31 mmol) and 8 equivalents of ICl (2.5 mmol) in MeOH (13 cm^3) was kept just below the boiling point for 24 h.

In the reaction of II (0.24 mmol) with just one equivalent of ICl (0.24 mmol) in CCl_4 (10 cm^3) at room temperature, II and IV were present in 77/23 ratio after 30 min and 46/54 ratio after 3 h (run 4 Table 1). In contrast, when the same mixture was kept in MeOH (10 cm^3) for 24 h little, if any, reaction took place (run 5 in Table 1).

It seems that the ICl promotes the ionization of the $TsiSiMe_2I$, possibly to form an ion pair $[(TsiSiMe_2)^+ (I_2Cl)^-]$ (the cationic portion is for simplicity represented as a simple ion, but is probably a bridged species), which can collapse to the chloride IV or, in MeOH, can in part react with the solvent (possibly after dissociation to separated ions) to form the methoxide III. Again, however, the solvent effects seem anomalous; the reaction apparently takes place much more readily in CCl_4 than in MeOH (though this might not be true at all concentrations of halogen, because the orders with respect to this component are likely to be different in the two media), whereas one might have expected methanol to facilitate reaction markedly by solvation of the transition state. We fall back with little enthusiasm on the suggestion that the tightness of the initially formed ion pair (partly formed in the transition state) does not allow much opportunity for solvation.

Iodine can also catalyse the reaction of II with MeOH, though much less effectively than ICl. When a solution of II (0.24 mmol) and I_2 (1.92 mmol) in MeOH (10 cm^3) was kept just below its boiling point for 24 h, ^{1}H NMR spectroscopy on the solution showed that III and II were present in 75/25 ratio. In the absence of the iodine only about 15% of the iodide would have been converted into the methoxide.

The reactions of I and II with INO_3 (generated from I_2 and $AgNO_3$) were briefly examined. When I (0.35 mmol) was treated with a molar equivalent of INO_3 (0.35 mmol) in MeOH (10 cm^3), a sample removed after 1 h at room temperature was shown by ^{1}H NMR spectroscopy (on the reaction solution) to contain only I and II, in 10/90 ratio. A similar procedure but with 8 equivalents of INO_3 (2.75 mmol) showed the presence of the methoxide III and the iodide II in 92/8 ratio, and after a total of 1.5 h only III was present. Similarly when the iodide II (0.24 mmol) was treated with 8 equivalents of INO_3 in MeOH (10 cm^3), after 1 h only III was present. It is noteworthy that unlike chloride ion from ICl, no nitrate ion from INO_3 is captured during the reaction with II. (In contrast there is some incorporation of nitrate ion during the reaction of II with $AgNO_3$ in MeOH, which is thought to proceed via a cation of type **B** [12], but the reaction with INO_3 does not, on our

TABLE 2

REACTIONS OF $TsiSiPh_2H$ (V) AND $TsiSiPh_2I$ (VI) WITH HALOGENS, XY

Run No.	Silane (mmol)	XY (mmol)	Solvent (cm^3)	Temperature (°C)	Time (h)	Product composition (%)
1	V (0.24)	ICl (0.24)	MeOH (5)	21	24	V 56; VI 28; VII 16
					72	V 51; VI 33; VII 16
2	V (0.24)	ICl (0.48)	MeOH (5)	21	24	V 37; VI 46; VII 17
					72	V 35; VI 44; VII 21
3	V (0.24)	ICl (1.93)	MeOH (10)	21	24	VI 35; VII 58; VIII 7
					48	VI 29; VII 63; VIII 8
4	V (0.24)	ICl (1.93)	MeOH (10)	ca. 60	4	VII 88; VIII 12
5	V (0.24	I_2 (0.24)	MeOH (13)	ca. 60	5	V 100
6	VI (0.19)	ICl (1.5)	MeOH (10)	21	12	VI 48; VII 40; VIII 12
					48	VI 17; VII 68; VIII 14
7	VI (0.19)	I_2 (1.5)	CCl_4 (10)	ca.75	5	VI 100

interpretation, involve actual nitrate ions.) A further feature of the results is that the reaction of the hydride I with INO_3 in MeOH to give II seems to be markedly slower than that with ICl, whereas the methanolysis of the iodide II is apparently more effectively catalysed by INO_3 than by ICl.

$TsiSiPh_2H$ (V) $(Me_2Si)_2C(SiPh_2Me)(SiMe_2OMe)$ (VII)

$TsiSiPh_2I$ (VI) $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$ (VIII)

We next turned to the reaction of $TsiSiPh_2H$ (V) and $TsiSiPh_2I$ (VI) with ICl. A solution of $TsiSiPh_2H$ (0.24 mmol) and ICl (0.24 mmol) in MeOH (5 cm^3) was stirred at room temperature (run 1 in Table 2). After 24 h, ^1H NMR spectroscopy showed that V, VI, and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$ (VII) were present in 56/28/16 ratio, and after 72 h the proportions were 51/33/16. (There was probably a little rearranged chloride VIII present, but not enough to be detected.) When 2 equivalents of ICl (0.48 mmol) were used under the same condition, the same products were present in 37/46/17 ratio after 24 h, and 35/44/21 ratio after 72 h (run 2 in Table 2). When 8 equivalents of ICl were used, but in 10 cm^3 of MeOH (run 3 in Table 2), no hydride V remained after 24 h, and the products were VI, VII and VIII in 35/58/7 ratio; after 48 h the proportions were 29/63/8. When a similar mixture was kept just below its boiling point for 4 h, none of the iodide VI remained, and VII and VIII were present in 88/12 ratio (run 4 Table 2), When a solution of the iodide VI (0.185 mmol) with 8 equivalents of ICl in MeOH (10 cm^3) was kept at room temperature, after 12 h VI, VII, and VIII were present in 48/40/12 ratio, and after 48 h in 17/68/14 ratio (run 6 in Table 2).

It is evident from the above results that $TsiSiPh_2H$ is much less reactive than $TsiSiMe_2H$ towards ICl, and that $TsiSiPh_2I$ is somewhat less reactive than $TsiSiMe_2I$ towards this reagent. Since in MeOH the reactivity difference between the two hydrides is greater than that between the iodides, whereas $TsiSiMe_2H$ can be converted virtually quantitatively into $TsiSiMe_2I$ by use of one molar equivalent of ICl, $TsiSiPh_2H$ gives a mixture of the iodide VI and the methoxide VII (and presumably a little of the chloride VIII).

An important feature of the reaction of $TsiSiPh_2I$ with ICl is that the products are the rearranged species VII and VIII, as would be expected if a cationic intermediate (presumably of type **B**) were produced by assisted ionization of the iodide [2]. In an attempt to produce the rearranged iodide $(Me_3Si)_2C(SiPh_2Me)(SiMe_2I)$, a solution of VI with 8 equivalents of I_2 in CCl_4 was kept just below the boiling point for 5 h, but no reaction took place (run 7 in Table 2).

In keeping with the lower reactivity of V than of I towards ICl, no reaction took place when a solution of V and one equivalent of iodine was kept at room temperature for 5 h (run 5 in Table 2), but under similar conditions reaction with Br_2, to give $TsiSiMe_2Br$, was complete within 4 min.

Experimental

Compounds I, II, V, and VI were prepared as previously described [1,2]. Authentic samples of compounds III, IV, VII and VIII were available [1,2,12].

Reactions of TsiSiMe$_2$H (I) or TsiSiMe$_2$I (II) with halogens

1. Involving isolation of products. (a) The colour was rapidly discharged when a solution of ICl (0.055 g, 0.345 mmol) in MeOH (3 cm^3) was added at room temperature (ca. 21°C) to a solution of I (0.10 g, 0.345 mmol) in MeOH (10 cm^3). (The sample of I was initially dissolved in a few drops of CCl$_4$ to aid dissolution in MeOH.) After 10 min the MeOH was rapidly evaporated off at room temperature under vacuum. The residue was shown to be exclusively TsiSiMe$_2$I by the identity of its ^{1}H NMR spectrum with that of an authentic sample.

The same result was obtained when CH$_3$CO$_2$H was used as solvent.

(b) When Br$_2$ was used in MeOH or CH$_3$CO$_2$H, in place of ICl, the colour disappeared within 4 min and the product was exclusively TsiSiMe$_2$Br.

(c) When I$_2$ was used under similar conditions in MeOH as solvent the iodine colour weakened only slowly. Work up after 2 h gave a mixture which was shown by ^{1}H NMR spectroscopy to contain TsiSiMe$_2$H and TsiSiMe$_2$I in ca. 60/40 ratio.

2. Involving in situ analysis of reaction mixtures by ^{1}H NMR spectroscopy. In the case of runs 1–5, 10 and 11 in Table 1, the reactions were monitored by removal of samples at various times and recording of the ^{1}H NMR spectra of the reaction mixtures. The proportions of the products were estimated from the heights of the peaks from the (Me$_3$Si)$_3$C or (Me$_3$Si)$_2$C protons of the various species. A typical procedure (Run 2, Table 1) was as follows.

A solution of I (0.10 g, 0.35 mmol) in two drops of CCl$_4$ was mixed with MeOH (10 cm^3), and a solution of ICl (0.45 g, 2.76 mmol) in MeOH (3 cm^3) was added. The mixture was stirred at room temperature, and at various times (see Table 1) samples were withdrawn and analyzed by ^{1}H NMR spectroscopy.

A different procedure was used for the reactions with iodine in runs 6–9 of Table 1. Normally a solution of iodine (0.345 mmol) in a given solvent (MeOH, CCl$_4$, or CH$_3$CO$_2$H) (5 cm^3) was mixed with a solution of TsiSiMe$_2$H (initially dissolved in a few drops of CCl$_4$) in the same solvent (10 cm^3). However, since I$_2$ was not sufficiently soluble in CF$_3$CO$_2$H alone, in this case the halogen in CCl$_4$ (3 cm^3) was mixed with a solution of I in anhydrous CF$_3$CO$_2$H (12 cm^3). After 5 h at room temperature an excess of 10% aqueous sodium thiosulphate was added, and the organosilicon material was extracted with CH$_2$Cl$_2$. The extracts were dried and evaporated and the I/II ratio was determined by ^{1}H NMR spectroscopy on a CCl$_4$ solution.

In run 12 of Table 1, a solution of I$_2$ (0.035 mmol) in CCl$_4$ (0.3 cm^3) was mixed with CF$_3$CO$_2$H (0.7 cm^3). The mixture was added to I (0.035 mmol) in an NMR tube and after shaking this tube was placed in the probe of the spectrometer (at 35°C). The spectrum recorded about 2 min after the mixing of the reactants showed I and II to be present in ca. 28/72 ratio, and on removal of the tube from the probe no iodine colour remained. The tube was returned to the probe, and a second spectrum recorded after a total reaction time of 6 min showed only II to be present.

In run 13 of Table 1, a solution of II (0.24 mmol) and I$_2$ (1.92 mmol) in MeOH (10 cm^3) was kept just below its boiling point for 24 h, and then examined by ^{1}H NMR spectroscopy, which showed II and III to be present in 25/75 ratio.

Treatment of TsiSiMe$_2$Cl with ICl

A solution of ICl (2.47 mmol) in MeOH (3 cm^3) was added to a solution of TsiSiMe$_2$I (0.31 mmol) (initially dissolved in a few drops of CCl$_4$) in MeOH (10

cm^3). The mixture was kept for 24 h at room temperature and then evaporated to give unchanged $TsiSiMe_2Cl$.

Reactions of I and II with INO_3

(a) A solution of INO_3 (0.35 mmol) was made from $AgNO_3$ (0.059 g) and I_2 (0.088 g) in MeOH (7 cm^3), and a solution of I (0.35 mmol) in MeOH (3 cm^3) was added. After 1 h at room temperature a sample of the solution was withdrawn and shown by ^1H NMR spectroscopy to contain only I and II in 10/90 ratio.

(b) A similar procedure but with 8 equivalents of INO_3 (2.75 mmol) showed that II and III were present in 8/92 ratio after 1 h, and after 1.5 h only III was present.

(c) A solution of II (0.24 mmol) in MeOH (3 cm^3) was mixed with a solution of INO_3 (1.92 mmol) in MeOH (10 cm^3) prepared as indicated in (a). After 1.5 h at room temperature only III was present.

Reactions of $TsiSiPh_2H$ (V) and $TsiSiPh_2I$ (VI) with halogens

1. Involving isolation of product or unchanged reactant. (i) A solution of Br_2 (0.35 mmol) in MeOH (2 cm^3) was added with stirring to a solution of $TsiSiPh_2H$ (0.35 mmol) in MeOH (8 cm^3). After 45 min (reaction may have been complete in a much shorter period) the solution was evaporated to give exclusively $TsiSiPh_2Br$, the identity of which was established by comparison of its ^1H NMR spectrum with that of an authentic sample.

(ii) In run 7 of Table 2, a solution of I_2 (1.5 mmol) in CCl_4 (5 cm^3) was mixed with a solution of VI (0.19 mmol) in CCl_4 (5 cm^3). The mixture was kept just below its boiling point for 5 h, then evaporated. The residue was shown by ^1H NMR spectroscopy to be unchanged VI.

(iii) In run 5 of Table 2, a solution of I_2 (0.24 mmol) in MeOH (3 cm^3) was added to a solution of V (0.24 mmol) in MeOH (10 cm^3). (To aid dissolution V was first dissolved in a few drops of CCl_4.) The mixture was kept just below its boiling point for 5 h, and the solvent was then evaporated to leave unchanged V.

(iv) In run 4 of Table 2, a solution of ICl (1.93 mmol) in MeOH (2 cm^3) was added to a solution of V (0.24 mmol) in MeOH (8 cm^3), The mixture was kept just below its boiling point for 4 h. Hexane (10 cm^3) was added, and the solution shaken with an excess of aqueous (10%) sodium thiosulphate to remove the residual ICl. The organic layer was washed with water then evaporated. The residue was shown by ^1H NMR spectroscopy to consist of VII and VIII in 88/12 ratio.

2. Involving in situ analysis of reaction mixtures by ^1H NMR spectroscopy. The procedure for runs 1–3 and 6 of Table 2 was essentially the same as for runs 1–5 of Table 1.

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