Journal of Organometallic Chemistry, 226 (1982) 143—148
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

HALOGEN REDISTRIBUTION REACTIONS BETWEEN ALKYL HALIDES AND TRIMETHYLSILYL IODIDE

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(Received August 11th, 1981)

Summary

Trimethylsilyl iodide has been found to react rapidly at 50°C with 1-fluorooctane, 2-fluorooctane and benzyl fluoride to produce the corresponding octyl or benzyl iodides and trimethylsilyl fluoride. Also, it reacts rapidly and cleanly with t-butyl chloride or bromide to form t-butyl iodide. However, it does not react readily with the 1-octyl, 2-octyl, benzyl or allyl chlorides or bromides. We have discovered that tetra-n-butylammonium iodide catalyzes the reactions of primary alkyl chlorides or bromides with trimethylsilyl iodide, and molecular iodine catalyzes the reactions of secondary and tertiary alkyl chlorides and bromides. However, tetra-n-butylammonium iodide slows down the reactions of secondary and tertiary alkyl chlorides and bromides. Mechanistic pathways are suggested for each of the various types of halogen redistribution processes encountered.

Introduction

In 1969, Nagai and coworkers [1] reported that triethylsilyl iodide reacted with alkyl chlorides or bromides under both photochemical and thermal conditions to form the corresponding alkyl iodides (eq. 1). However, the reactions

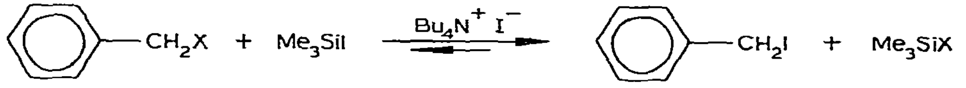
$$\mathrm{Et_3SiI} + \mathrm{RX} \xrightarrow[\mathrm{X=Cl,Br}]{h\nu \text{ or } \Delta} \mathrm{Et_3SiX} + \mathrm{RI} \qquad (1)$$

were slow and most of the yields were low. The orders of reactivity they observed for the alkyl halides were tertiary > secondary > primary and bromides > chlorides. Based on this and related evidence, they suggested that both the photochemical and thermal processes might involve free-radical chain mechanisms. However, they noted that benzoyl peroxide did not act as a catalyst.

Recently, as part of a study of trends in Group IVA metal—halogen bond dissociation energy differences, a brief examination of various halogen redistribution reactions between alkyl halides and trimethylsilyl iodide were reported

0022-328X/82/0000—0000/$02.75

from our laboratory [2]. In this investigation it was found that in the presence of a catalytic amount of tetra-n-butylammonium iodide halogen redistributions with benzyl chloride or bromide proceeded readily and gave equilibrium mixtures strongly predominating in benzyl iodide (eq. 2). However, simple primary, secondary, and tertiary alkyl chlorides and bromides were found to possess very low reactivity in the presence of the tetra-n-butylammonium iodide catalyst.



(2)

(X = Cl , Br)

We now wish to report our results from more detailed studies of the reactions of trimethylsilyl iodide with alkyl halides. These were done in connection with our continuing interests [3,4] in halogen redistribution reactions between alkyl halides and Group IVA trialkylmetal halides. Our initial objectives were to search for reaction conditions or catalysts which would enable the trimethylsilyl iodide-alkyl halide halogen redistributions to be carried out conveniently using a wide variety of substrates.

Results

In the early stages of our search for possible ways to extend the generality of halogen redistribution reactions between alkyl halides and trimethylsilyl halides, we examined the catalytic behaviors of various free-radical initiators and inhibitors and Lewis acids and bases upon the reaction of trimethylsilyl iodide with benzyl chloride. With most of the additives, little or no effects upon the rate of reaction were observed. However, we were gratified to discover that small amounts of molecular iodine did exhibit a rate accelerating catalytic effect. With benzyl chloride the catalytic effect of iodine was similar in magnitude to that observed earlier for tetra-n-butylammonium iodide [2]. On the other hand, for the reaction of benzyl bromide with trimethylsilyl iodide the catalytic effect of tetra-n-butylammonium iodide was found to be much greater than that of iodine.

To learn more about the catalytic behaviors of iodine and tetra-n-butylammonium iodide, we systematically examined the halogen redistribution reactions of trimethylsilyl iodide with the 1-octyl, 2-octyl, t-butyl, benzyl, and allyl halides using both catalysts. Selected alkyl fluorides as well as bromides and chlorides were included in the study. A summary of the results is given in Table 1.

An initially unexpected result was the observation that the 1-octyl, 2-octyl and benzyl fluorides all reacted rapidly at 50°C with trimethyl iodide to give the corresponding alkyl iodides and trimethylsilyl fluoride even in the absence of a catalyst. Corresponding reactions of t-butyl fluoride or allyl fluoride were not examined owing to volatility problems which would necessarily be encountered in working with these materials. However, it is felt that they should have similar high reactivities as the fluorides we examined.

The data in Table 1 clearly illustrate the catalytic activity of molecular

TABLE I

ESTIMATED TIMES FOR 50% OF THEORETICAL ALKYL IODIDE FORMATION IN THE REACTIONS OF VARIOUS ALKYL HALIDES WITH TRIMETHYLSILYL IODIDE [a,b]

Alkyl halide		Time (h) for 50% reaction with various additives [c]		
R	X	None	I_2	Bu_4NI
1-Octyl	F	2.5	<0.1	0.5
	Cl	[d]	[d]	[d]
	Br	[d]	[d]	70
2-Octyl	F	<0.1	<0.1	<0.1
	Cl	300	40	[d]
	Br	900	100	[d]
t-Butyl	Cl	1.5	0.1	200
	Br	1.5	0.1	125
Benzyl	F	0.5	<0.1	<0.1
	Cl	45	0.5	0.5
	Br	55	2	<0.1
Allyl	Cl	600	140	7
	Br	70	20	<0.1

[a] The RX/Me_3SiI mole ratio was 1/1 in each case. [b] All reactions were carried out neat and at 50°C. [c] Five mole % of I_2 or Bu_4NI was used. [d] Less than 1% reaction in 100 h.

iodine. However, it is interesting to note that the t-butyl chloride and bromide react rapidly even in the absence of a catalyst. The place where the catalytic effect of iodine is most noteworthy is in the 2-octyl system where the chloride and bromide have convenient reactivities only when using the iodine catalyst. Besides the examples shown in Table 1, iodine catalyzed runs were also carried out with the cyclopentyl and cyclohexyl chlorides or bromides which qualitatively showed similar accelerations in rate.

Although all of the iodine catalyzed halogen redistributions proceeded in high yields to form the alkyl iodides, there is some evidence that the reactions of the tertiary and thus possibly also the secondary alkyl halides involve at least in part a hydrogen halide elimination-readdition process. This evidence comes primarily from an iodine catalyzed 1/1/1 mole ratio reaction of t-butyl chloride with trimethylsilyl iodide in the presence of 1-methylcyclohexene to scavenge any eliminated hydrogen halide by forming 1-iodo-1-methylcyclohexane. Under these conditions conversion of the t-butyl chloride to the iodide was accompanied by about 18% isobutene formation, whereas none was observed in the absence of 1-methylcyclohexene.

Unfortunately, even using the molecular iodine catalyst, the primary 1-octyl chloride and bromide still reacted very slowly. In fact in the presence of iodine the rates were even slower than in the presence of a catalytic amount of tetra-n-butylammonium iodide. A similar behavior is observed with the allyl and benzyl chlorides and bromides where the reaction rates were more rapid using a tetra-n-butylammonium iodide catalyst than using an iodine catalyst. However, it is interesting to note that with the 2-octyl and t-butyl chlorides and bromides the addition of tetra-n-butylammonium iodide actually appears to slow down their reactions with trimethylsilyl iodide over those in the absence of any catalyst.

The high reactivities of the alkyl fluorides relative to the corresponding alkyl chlorides or bromides encountered in this work can be explained by a mechanism involving trimethylsilyl iodide acting as a Lewis acid in assisting carbon—fluorine bond breaking [5,6]. Whether the overall reaction in the absence of a catalyst proceeds stepwise through a carbocation intermediate or in one step involving a nucleophilic attack by iodide ion or some iodide containing species upon the trimethylsilyl iodide coordinated alkyl fluoride would depend upon the specific alkyl fluoride involved.

For the various halogen redistribution processes studied the accelerating catalytic effect of tetra-n-butylammonium iodide was found to be larger than that of molecular iodine only with the primary 1-octyl, benzyl and allyl halide systems. This, together with the observation that for the primary alkyl halides the bromides are more reactive than the chlorides, suggests that the tetra-n-butylammonium iodide catalyzed reactions with the primary alkyl halides must involve bimolecular backside displacements. It is believed that the nucleophile in the rate-determining step is probably iodide ion. However, an iodide coordinated trimethylsilyl iodide nucleophile has not been completely ruled out.

The observation that with the 2-octyl and t-butyl chlorides and bromides the addition of tetra-n-butylammonium iodide actually appears to slow down their reactions with trimethylsilyl iodide is most intriguing. However, a possible explanation we can suggest for this behavior is that the uncatalyzed reactions may all involve a rapid preequilibrium such as that shown below (eq. 3) whose

$$RX + Me_3SiI \rightleftharpoons R{-}\overset{+}{X}{-}SiMe_3 + I^- \qquad (3)$$

position is shifted unfavorably by the addition of iodide ion. The differential action of iodide ion with the primary versus the secondary and tertiary alkyl halides may then be because with the primary alkyl halides a facile direct nucleophilic displacement on alkyl halide by iodide ion reaction mechanism is available even when the alkyltrimethylsilyl halonium iodide pathway is suppressed. With the secondary alkyl halides direct nucleophilic displacement is much less favorable, and with the tertiary alkyl halides it is virtually non-existent. Thus, with these systems the alkyltrimethylsilyl halonium iodide pathway becomes relatively much more important.

Support for the postulated preequilibrium in the reactions of the alkyl halides with trimethylsilyl iodide also comes from the behavior observed in the molecular iodine catalyzed reactions. Thus, in the presence of molecular iodine the order of alkyl halide reactivity is tertiary > secondary > primary. Also, at least for the secondary and tertiary systems, the chlorides are more reactive than the bromides. These orders of reactivity suggest a Lewis acid assisted alkyl halide ionization process in the rate-determining step with trimethylsilyl iodide acting as the Lewis acid. If this involves formation of an alkyltrimethylsilyl halonium iodide species in a preequilibrium step, a likely explanation for the catalytic action of iodine is in shifting the equilibrium position to the right by tying up the iodide ion as triiodide [7]. For the secondary and tertiary alkyl halides the reaction then proceeds to a carbocation intermediate which upon reaction with triiodide regenerates the iodine. This is shown in Scheme 1.

Work is continuing on an investigation seeking to learn more about the cata-

SCHEME I

$$RX + Me_3SiI \rightleftharpoons R\text{—}\overset{+}{X}\text{—}SiMe_3 + I^-$$

$$I^- + I_2 \rightleftharpoons I_3^-$$

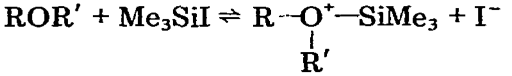
$$R\text{—}\overset{+}{X}\text{—}SiMe_3 \rightarrow R^+ + XSiMe_3$$

$$R^+ + I_3^- \rightarrow RI + I_2$$

lytic effects of iodine and of iodide ion in the reactions of trimethylsilyl iodide with alkyl halides and also with other systems. Thus, it is believed that extensions of the mechanisms uncovered in the present study may lead to an understanding of the catalytic effects of iodine or iodide ion in other reactions involving organosilicon reagents. For example, Benkeser and coworkers [8a] and Olah and coworkers [8b] have reported molecular iodine accelerations of cleavages of both esters and ethers with trimethylsilyl iodide. Benkeser [8a] has suggested that the function of iodine may be to coordinate with the trimethylsilyl iodide giving a triiodide—silicon bond (eq. 4) which is more polarizable

$$Me_3SiI + I_2 \rightleftharpoons Me_3\overset{\delta_+}{Si}\text{—}\overset{\delta_-}{I_3} \tag{4}$$

than iodide—silicon. However, a mechanism similar to that proposed in the present work is also possible. This would involve a preequilibrium forming a trimethylsilyloxonium iodide species from the ether or ester (eq. 5) which is



$$ROR' + Me_3SiI \rightleftharpoons R\text{—}\underset{\displaystyle R'}{\underset{|}{O^+}}\text{—}SiMe_3 + I^- \tag{5}$$

shifted to the right through triiodide formation by iodine. On the other hand, we do not have a ready explanation at present for the related reports of Olah and coworkers [9a] and Hanessian and Guidan [9b] that iodide ion catalyzes cleavages of ethers using organosilicon reagents, but does not catalyze corresponding cleavages of esters even when they are primary.

Experimental

Materials

The various alkyl chlorides and bromides employed in the present work were obtained commercially and, if necessary, distilled before use. 1-Fluorooctane was prepared in 32% distilled yield by the reaction of potassium fluoride dihydrate and 1-bromooctane in triethylene glycol solvent; b.p. 38—40°C/12 mmHg, $n_D^{23.5}$ 1.3956 (lit. [10] b.p. 142.5°C/760 mmHg, n_D^{20} 1.3945). 2-Fluorooctane was prepared in 11% distilled yield by the reaction of anhydrous potassium fluoride and 2-octyl tosylate in triethylene glycol solvent, b.p. 55—57°C/ 41 mmHg, n_D^{22} 1.3941 (lit. [11] b.p. 139—140°C/760 mmHg, n_D^{20} 1.3927). Benzyl fluoride was prepared in 43% yield by the reaction of potassium fluoride dihydrate with benzyl chloride in triethylene glycol solvent, b.p. 48°C/ 25 mmHg, n_D^{20} 1.4933 (lit. [12] b.p. 55—56°C/30 mmHg, $n_D^{25.3}$ 1.48919). Trimethylsilyl iodide was prepared in 66% distilled yield by the reaction of hexamethyldisiloxane [13] and iodine in the presence of aluminum turnings, b.p. 103—106°C/760 mmHg. (lit. [14] b.p. 106°C/760 mmHg).

General procedure for runs

All reactions were carried out on millimole scale in tightly capped or sealed NMR tubes. In each case, solids were weighed directly into the tubes and liquids were weighed out in syringes. The reaction mixtures were heated at 50 ± 3°C in an oil bath (except for those cases where reaction appeared to be essentially instantaneous) and periodically removed for direct proton NMR examination without any prior workup. The course of the reactions were followed by integrating the appropriate alkyl halide α-proton and/or trimethylsilyl halide methyl proton absorption. The chemical shifts for the latter, which varied slightly in different reaction mixtures, were approximately 0.9 ppm for the iodide, 0.6 ppm for the bromide, 0.4 ppm for the chloride, and 0.1 ppm for the fluoride. The approximate chemical shifts for the alkyl chloride, bromide and iodide absorptions used in the analyses were reported earlier [15]. The chemical shifts of the α-proton absorptions used for the alkyl fluoride analyses were: 1-fluorooctane 4.2 ppm, 2-fluorooctane 4.3 ppm, and benzyl fluoride 5.3 ppm. The estimated times for 50% alkyl iodide formation given in Table 1 were obtained by extrapolating results which bracketed 50% reaction or, in the case of the very slow reactions, which lead toward 50% reaction *.

Acknowledgement

This research was supported in part by a Faculty Research Grant from the Committee on research of the University of California, Davis.

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* *Note added in proof.* Olah, Narang and Field [16] have just reported their independent discovery of the uncatalyzed reactions of primary, secondary, or tertiary alkyl fluorides and of tertiary alkyl chlorides with iodotrimethylsilane to give the corresponding alkyl iodides in high yields.