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REAGENTS AND SYNTHETIC METHODS 52. SILANE REDUCTION OF CARBONYL COMPOUNDS IN THE PRESENCE OF IODINE.

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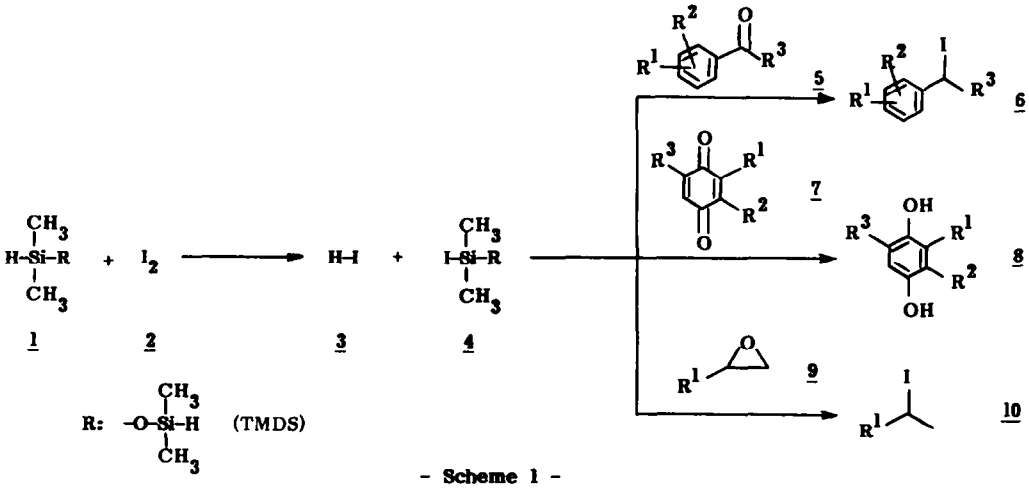
Abstract: Synthetic utility of 1,1,3,3-tetramethyldisiloxane (TMDS) reagent under the influence of iodine is described. TMDS reagent in combination with iodine produces alkyl iodides from carbonyl compounds and oxiranes in good to excellent yields. Reduction of quinones into hydroquinones is also described. The mentioned transformations are explained from mechanistic points of view.

The use of organosilicon reagents became significant during recent years in organic synthesis[1,2]. An important class of these reagents involves the use of silicon hydrides as reducing agents[1-4]. Recently, we have preliminarily reported the synthetic utility of 1,1,3,3-tetramethyldisiloxane (TMDS) 1 together with iodotrimethylsilane, generated from chlorotrimethylsilane and sodium iodide, for the preparation of benzyl halides from benzaldehydes[5] and alkyl halides from oxiranes[6]. In view of the synthetic interest of this new reductive halogenation method, we were interested in developing other methods for the "in situ" generation of halosilanes or their equivalents. A number of years ago, it was established that hydrosilanes 1 react with iodine 2 to produce hydriodic acid 3 and the corresponding halosilane 4, however, synthetic application of this system has been very little investigated[7]. This lead us to utilize this simple and inexpensive alternative of iodine together with 1,1,3,3-tetramethyldisiloxane (TMDS) reagent for generating the required iodosilane species. It is the purpose of this paper to give a more detailed account of this new reductive halogenation method and to present some new applications of the reaction to ketones and quinones.

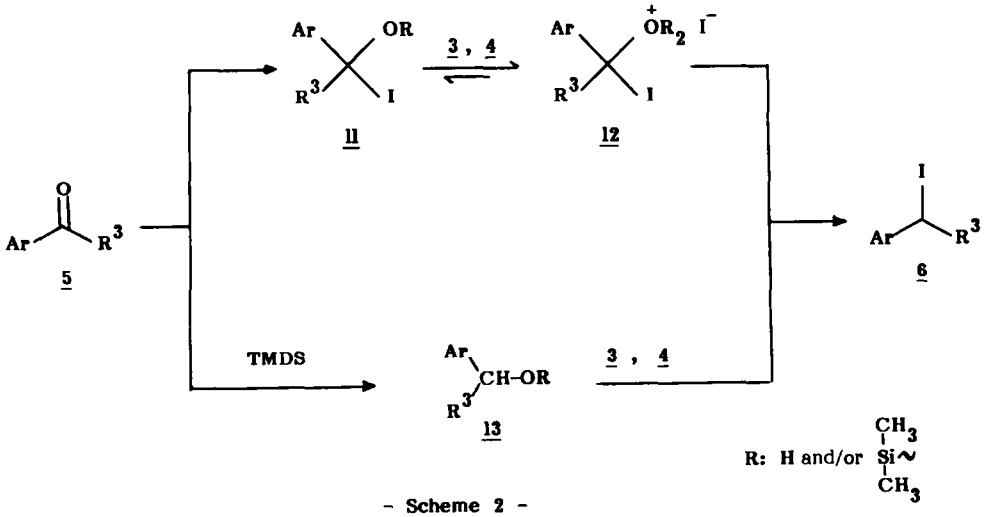


- Scheme 1 -

Haloreduction of carbonyl compounds: Concerning silane reductions of carbonyl groups, Doyle et al[8] have reported the reduction of aldehydes and ketones to hydrocarbons, alcohols, symmetrical ethers, esters, and acetamides. Corriu and coworkers[9] have described that potassium or caesium fluoride induced hydrosilylation of carbonyl compounds into alcohols. Also, Fujita and coworkers[10a] treated aldehydes and ketones with hydrosilanes in the presence of a catalytic amount of tetrabutylammonium fluoride to obtain the corresponding alcohols, and more recently, Fry et al.[10b] have studied the fluoride ion promoted reaction of (R)-α-naphthylphenylmethylsilane with several prochiral ketones. Homogeneous rhodium (I) or ruthenium (II) also were used as catalysts for hydrosilylation of 4-t-butylcyclohexanone[11] and Lewis acids also have been reported to be quite suitable as catalysts for hydrosilylation reactions[12].

Recently, we have preliminarily reported[5] that 1,1,3,3-tetramethyldisiloxane (TMDS) 1 together with iodotrimethylsilane allows direct reductive halogenation of aromatic aldehydes 5 into benzyl iodides 6. Thus, the halide groups were smoothly formed by treatment of benzaldehydes 5 with the reagent 1 and sodium iodide in anhydrous acetonitrile in the presence of chlorotrimethylsilane in a molar ratio 1: ArR^3CO:NaI: $ClSiMe_3$ = 1: 1: 1.5: 1.5. In this way, the halide compounds were formed in high yields and short reaction times. However, we have found that the method, as described, was not generally applicable, since the examples reported concerned only aldehydes of type ArCHO. Reaction between ketones such as 4-methylacetophenone and cyclohexanone, sodium iodide/ chlorotrimethylsilane and TMDS reagent was found troublesome and difficult to control, giving mixtures of products in which we have detected by GLC and NMR analysis the corresponding ethers, alkanes and traces of the respective iodides. Our new finding is that aldehydes and ketones are easily reduced by TMDS reagent into alkyl iodides 6 in the presence of iodine. Thus, benzyl iodides 6 were formed in high yields by treatment of carbonyl compounds 5 with the reagent 1 and iodine in dichloromethane in a molar ratio 1: 1: 0.6 respectively. In general, the reaction is completed within 10min at room temperature and only one product was detectable by TLC analysis of the crude reaction mixture. The products 6 can be conveniently prepared in good yields by TMDS reduction under the influence of iodine. With the exception of alkyl aldehydes and ketones, aryl aldehydes and aryl ketones form benzyl iodides in yields greater than 70%. With carbonyl compounds containing carboxylate or cyano functional groups, only the carbonyl group is reduced. In both cases, pyridine was also used in order to neutralize the hydriodic acid 3 formed during the reaction. From 4-methoxybenzaldehyde and 4-ethoxycarbonylbenzaldehyde only the corresponding iodides were obtained and neither ether nor ester cleavage was produced under these reaction conditions. However, when the reaction was tested with aliphatic aldehydes such as n-heptanal, only the corresponding symmetrical ethers were formed in greater than 80% yield.

The halide formation can be explained by the reduction of an halohydrin intermediate[13] 11 or through an intermediate alcohol which easily undergoes the displacement of the hydroxyl group giving the alkyl iodide.



- Scheme 2 -

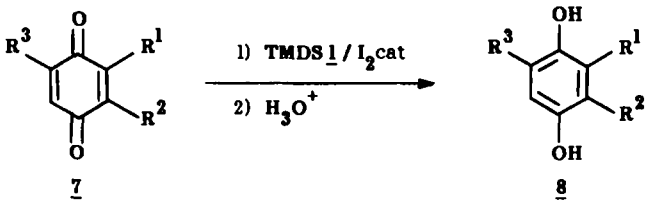
Formation of symmetrical ether followed by ether cleavage was rejected because we found that dibenzyl ether was cleaved in 1,2-dichloroethane under reflux conditions (80ºC) in 50% extention for 60min and in quantitative yield in 240min of reaction . In contrast - see Table 1 - benzyl iodide was formed in 80% yield at room temperature for 10min. A further feature of the method is worthy of note: direct halogenation of carbonyl group in aldehydes and ketones gives gem-dihalides by the literature procedures[14], but our method presents a high efficient direct synthesis of monoalkyl iodides from carbonyl compounds.

Table 1. Haloreduction of carbonyl compounds 5

Entry[a]	R^1	R^2	R^3	time[b] (min)	Yield (%)	m.p.ºC or b.p.ºC/torr found	reported	^{1}H-NMR δ ppm
1	H	H	H	10	80	140/4	25[21]	7.03(s,5H,arom.), 4.19(s,2H,CH_2)[c]
2	H	2-Cl	H	10	72	90/0.05	26-27[22]	7.01(m,4H,arom.),4.29(s,2H,CH_2)[c]
3	H	3-OH	H	5	87	80-82	—[d]	6.73-6.03(m,4H,arom.),3.95(s,1H, OH),3.90(s,2H,CH_2)[e]
4	2-CH_3	4-CH_3	H	8	83	95/0.02	—[d]	7.03-6.64(m,3H,arom.),4.20(s,2H, CH_2),2.17(s,6H,CH_3)[e]
5	H	4-CH_3	H	10	70	46-47	46[21]	6.92(d,d,4H,arom.),4.27(s,2H,CH_2) 2.20(s,3H,CH_3)[e]
6	H	4-CH_3O	H	10	66	105/0.02	27[21]	7.09,6.58(A_2B_2syst.,4H,arom), 4.31(s,2H,CH_2),3.61(s,3H,CH_3O)[c]
7	H	4-CN	H	15	75	140-144	143-144[23]	7.23(m,4H,arom),4.23(s,2H,CH_2)[e]
8	h	4-CH_3O_2C	H	45	75	73-74	76-77[24]	7.6,7.06(A_2B_2syst,4H,arom),4.18 (s,2H,CH_2),3.66(s,3H,CH_3O)[c]
9	H	H	CH_3	5	76	55/0.06	80/2[25]	6.9(m,5H,arom),5.03(q,1H,CH), 1.94(d,3H,CH_3)[c]
10	4-CH_3	H	CH_3	20	65	90/0.5	—[d]	6.97(m,4H,arom),5.15(q,1H,CH), 2.00(d,3H,CH_3)[e]

a) Molar ratio: substrate/I_2/1 = 1/0.6/1 ; for entries 6,7 and 8, molar ratio: substrate/I_2/Pyr/1 = 1/1.2/0.6/1 ,
b) Solvent: dichloromethane, room temperature ; for entries 7 and 8, solvent: 1,2-dichloroethane, reflux,
c) Spectra recorded in CCl_4, d) Characterized by comparison with authentic samples prepared by conventional procedures, e) Spectra recorded in $CDCl_3$.

Reduction of p-quinones: Conversion of hydroquinones to p-quinones and the reverse reaction are two important operations in organic synthesis because their structures are encountered in many naturally occurring substances. Various conventional reducing agents have been employed to convert quinones into dihydric phenols[15]; however, these procedures are generally accompanied by the concomitant formation of large amount of inorganic salts. Other methods described involve the silylation technique , and for this purpose various methods have been developed. Chlorotrimethylsilane[16a,b], bis(trimethylsilyl)mercury[16c,d], 1,2-difluorotetramethyldisilane[16e] and hexamethyldisilane[16f] are silyl reagents used to convert p-quinones into bis(1,4-trimethylsiloxy)benzenes. In some of these methods the reaction takes place only in the presence of metals[16b,c], involving forceful conditions and the yields being in the range 40 to 60%[16b,d,e]. Some of these reagents are also expensive, and thus, their application is limited. Kursanov and coworkers[17], have reported the reduction of benzoquinone to hydroquinone using triethylsilane in trifluoroacetic media. Because of the good yield reported for this silane reduction, we expected that TMDS reduction of benzoquinones under the influence of iodine would represent a convenient and synthetically useful method for transforming quinones into hydroquinones.



7 8

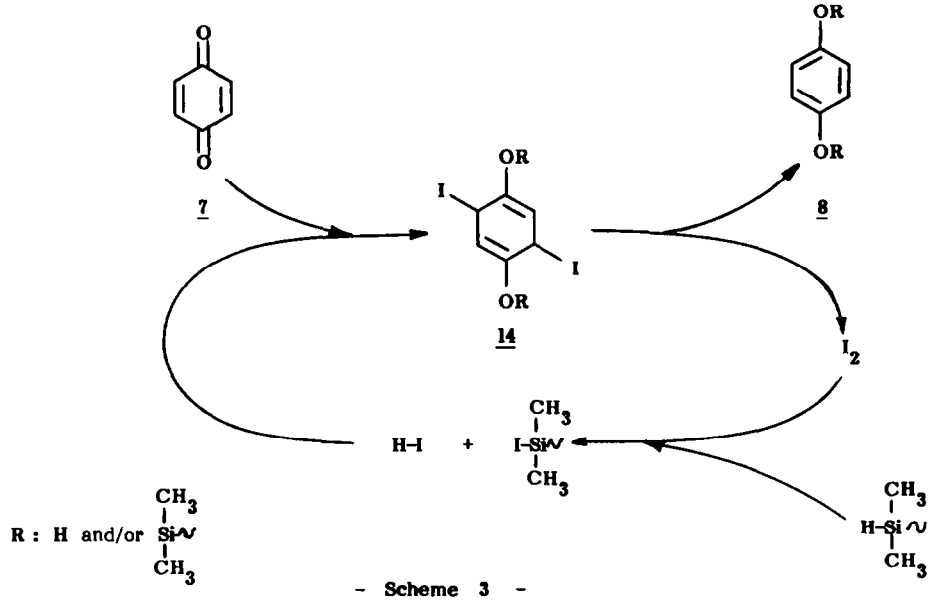
Table 2. Iodine catalyzed reduction of p-quinones 7

7[a]	R^1	R^2	R^3	% Yield	m.p. °C found	m.p. °C reported[26]
a	H	H	H	96	169-171	171
b	CH_3	CH_3	CH_3	90	168-171	169-172[b]
c	CH_3	H	H	90	123-126	124-126
d	Cl	H	H	85	99-102	106
e	CH_3O	H	H	98	88-95	90-92[b]
f	1,4-naphthoquinone			80	175	176

a) Molar ratio quinone 7/TMDS = 1/1 . b) All compounds were identified by their physical properties and by comparison with authentic samples (Fluka).

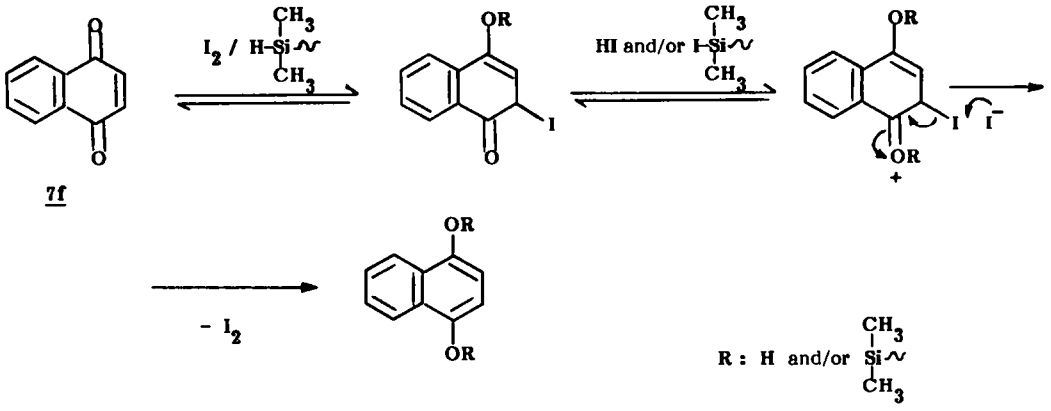
Reductions were carried out in refluxing dichloromethane for 30-35min, by using TMDS and iodine as catalyst. Conversion can be considered complete when the iodine violet colour disappears, aproximatively in 15min. As shown by the data listed in Table 2 , this procedure furnish a new general route to dihydric phenols from quinones in nearly quantitative yields. Furthermore, whereas 1,4-naphthoquinone was reduced into 1,4-dihydronaphthalene under triethylsilane/trifluoroacetic acid conditions[17], by our method only the expected 1,4-dihydroxynaphthalene was obtained in 80% yield.

In an attempt to explain the catalytic effect of iodine, we have observed that the reaction does not take place in its absence. As a possible reaction pathway for hydroquinone reduction, we suggest the formation of an intermediate such as 14 (Scheme 3) which is readily aromatized to the hydroquinone 8.



- Scheme 3 -

Scheme 4 shows an alternative reaction mechanism for reduction of 7 into 1,4-dihydroxynaphthlane, which appears to be applicable for all quinones tested.

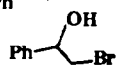
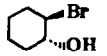
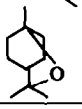
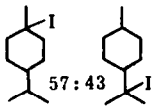


- Scheme 4 -

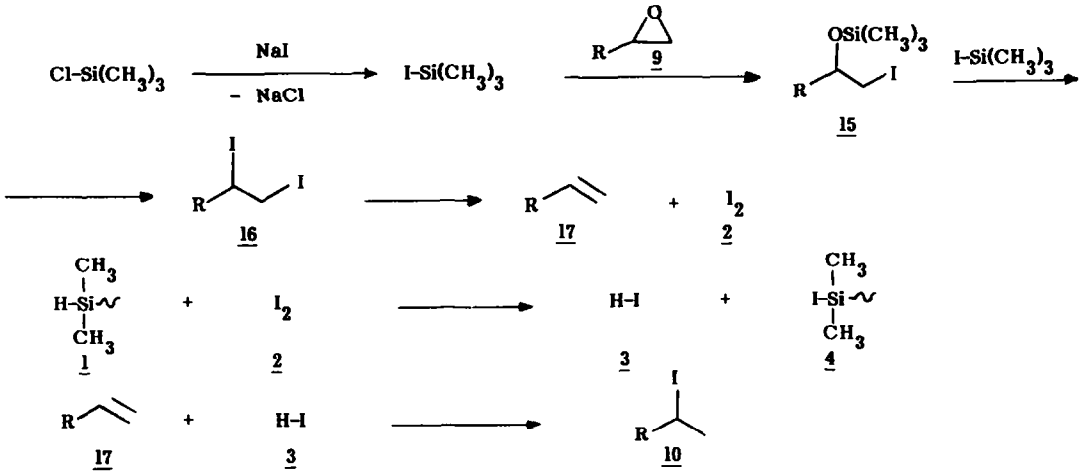
Haloreduction of oxiranes: Several studies have revealed that halotrimethylsilanes react with epoxides to form beta-si loxyalkylhalides under mild conditions[18]. Recent works showed the preparation of allylic alcohols from epoxides and iodotrimethylsilane[18a] or trimethylsilyl trifluoromethanesulfonate[18d]. Denis and Krief[19] have described the formation of olefins from epoxides and iodotrimethylsilane together with triethylamine, and Fry et al[20] have reported the reduction of epoxides to hydrocarbons by means of triethylsilane and boron trifluoride. In a preliminary communication[6] we have reported that reaction between epoxides and TMDS reagent in combination with sodium iodide/chlorotrimethylsilane gives alkyl iodides in good yields. Haloreductions were carried out in acetonitrile under reflux conditions, from equimolecular amounts of the corresponding oxirane and TMDS reagent in the presence of sodium iodide/chlorotrimethylsilane. The conversion was monitored by TLC analysis of the reaction mixture and the work-up was simple. Thus, when the reaction was complete, the remaining siloxane products were destroyed by adding 45% hydrofluoric acid in methanol under reflux conditions before distillation.

In view of the results above described, we next examined this haloreduction method by means of TMDS reagent together with iodine as source of iodosilane species or its equivalent and have found similar results. Thus,under the same conditions to those used in the reductive halogenation of aldehydes, various oxiranes are converted into iodides in good to excellent yields. Some examples are given in Table 3, and exceptionally, under these conditions, epoxypropane gives propene as only reaction product (the evolved gas was trapped with bromine and characterized as 1,2-dibromopropane). On the other hand, when epoxystyrene was allowed to react with TMDS reagent and lithium bromide/trimethylchlorosilane instead of NaI/$ClSiMe_3$ in trifluoroacetic acid media, 1-phenyl-2-bromoethane was isolated as only reaction product. Examination of this reaction with cyclohexene oxide in acetonitrile gave the corresponding bromohydrin, even after prolonged reflux. These results have significance in order to formulate a possible reaction mechanism (Scheme 5). Thus, sodium iodide together with chlorotrimethylsilane in acetonitrile affords iodotrimethylsilane[18a] which then reacts with the oxirane 9 to give the iodohydrin trimethylsilyl ether[19] 15. Reaction of 15 with iodotrimethylsilane leads to the formation of the diiodo compound 16, which loses iodine and gives the corresponding alkene 17 . Electrophilic addition of hydriodic acid 3 formed from iodine and TMDS reagent, affords the alkyl iodide 10 . In fact, we have proved that alkenes react with TMDS/iodine system in dichloromethane to afford the corresponding iodides (e.g., styrene, cyclohexene and methyl cinnamate give respectively 1-iodo-1-phenylethane (89%), iodocyclohexane (97%) and methyl 3-iodo-3-phenylpropanoate (90%).

Table 3. Reductive halogenation of epoxides 9.

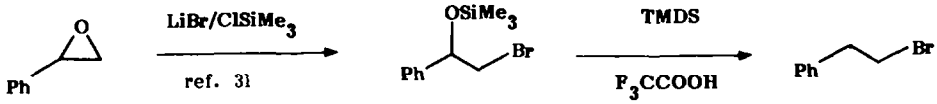
Entry	9	Reagents	time	Products	Yield[a]	m.p.ºC or b.p.ºC/torr		^{1}H-NMR (CCl_4)
						found	reported	δ ppm
1		NaI[b]	45min		76	80-84/0.15	70-80/2[25a]	6.90(m,5H,arom.)5.03 (q,1H,CH),1.94(d,3H, CH_3).
2		I_2[c]	10min		62	70/0.1		
3		LiBr[d]	15 h		69	220-5/760	217-8/760[25a]	see experimental
4		LiBr[b]	1.5 h		73	140-7/5	109-10/2[25b]	7.11(s,5H,arom.),5.72(m, 1H,CH),4.09(s,1H,OH), 3.65(d,2H,CH_2).
5		NaI[b]	30min		75	180-3/760	179/760[27]	4.18(m,1H,CH),1.90(m, 4H,CH_2),1.45(m,6H, CH_2)
6		I_2[c]	10min		100	180-5/760		
7		LiBr[a]	7h		93	195-200/760	88-90/33[28]	see experimental
8		I_2[c]	10min		90[e]	143/760	56-58/20[29]	4.06(m,1H,CH), 3.20-1.42(m,8H,CH_2).
9		NaI[b]	6h		86[f]	—	—	
10		NaI[b]	20min	 57 : 43	80[g]	—	—	

a) Yield of isolated pure products, the purity as determined by GLC and TLC analysis was 97% . b) From method A in experimental section, acetonitrile as solvent . c) From method B in experimental section, dichloromethane as solvent. d) Trifluoroacetic acid as solvent. e) Contaminated with siloxane products. f) Characterized as 1,2-dibromopropane. g) Conversion determined by GLC analysis.



- Scheme 5 -

In the case of the reaction between epoxystyrene , LiBr/$ClSiMe_3$ and TMDS in trifluoroacetic acid, the formation of 1-phenyl-2-bromoethane can be explained by the reduction of 1-phenyl-1-trimethylsiloxy-2-bromoethane



This result is in agreement with the report of Carey et al[30] in which the hydrosilane reduction of tertiary alcohols and secondary benzyl alcohols in trifluoroacetic acid media gives the corresponding alkanes. Finally, when epoxystyrene was allowed to react with TMDS reagent and LiBr/ClSiMe$_3$ in acetonitrile as solvent, 1-hydroxy-1-phenyl-2-bromoethane was isolated as only reaction product, and cyclohexene oxide gave trans--hydroxy-2-bomocyclohexane, according to the results reported by Kricheldorf[31,32].

Conclusions

The method described here presents a new reductive halogenation procedure for the direct conversion of benzaldehydes, some ketones and epoxides to alkyl iodides and a mild catalytic procedure for the conversion of quinones into hydroquinones, offering a great versatility from synthetic points of view as demonstrated here by a rather limited number of examples, which can be readily extended to further applications.

EXPERIMENTAL

Melting points were determined on a Büchi SMP-20 melting point apparatus and are uncorrected. Proton NMR spectra were measured on a Varian EM-360 Spectrometer and are reported in parts per million downfield from internal tetramethylsilane. All the starting materials used in this work were either commercially available in generally 98% or higher purity and used without further purification or preparated by standard literature procedures. Acetonitrile was purified by the usual methods and stored over molecular sieves. 1,1,3,3-tetramethyldisiloxane (TMDS) reagent was obtained from Wacker-Chemie GMBH (München, Germany).

General procedure for the haloreduction of carbonyl compounds.

A solution of 1,1,3,3-tetramethyldisiloxane (1.79ml, 10mmol) in dichloromethane (6ml) is dropwise added to a cooled mixture (-5ºC) of the corresponding carbonyl compound **5** (10mmol), iodine (1.52g, 6mmol) and dichloromethane (6ml) giving an exothermic reaction . In general, the reaction is completed within 10-15min. Then, the mixture is taken up over dichloromethane (30ml) and washed with water and saturated $NaHCO_3$ solution. Drying and evaporation of the solvent yields crude benzyl iodide **6** and siloxane compounds. The upper siloxane layer is separated and the lower one is purified by Kugelrohr distillation or recrystallization from hexane or hexane/tetrachloromethane.

4-Carbomethoxybenzyl iodide, Typical procedure.

A solution of TMDS (1.79ml, 10mmol) in 1,2-dichloroethane (6ml) is dropwise added to a cooled mixture (-5ºC) of 4-carbomethoxybenzaldehyde (1.64g, 10mmol), pyridine (0.5ml, 6mmol) and iodine (1.52g, 6mmol) in 1,2-dichloroethane (6ml), and the reaction mixture is refluxed for 45min. On completion, the mixture is taken up over dichloromethane (30ml) and washed with water (20ml x 2), 6N HCl (20ml x 2) and saturated $NaHCO_3$ solution. Drying and evaporation of the solvent yields crude solid 4-carbomethoxybenzyl iodide and liquid siloxane compounds. Purification of the crude mixture by crystallization from hexane affords the title compound (2.14g, 78%). m.p.: 73-74ºC (lit. m.p.: 76-77ºC)[24].

Haloreduction of oxiranes. Typical procedure for Method A. Cyclohexyl iodide.

A mixture of cyclohexene oxide (1.01ml, 10mmol), sodium iodide (2.00g, 13.3mmol) and trimethylchlorosilane (1.92ml, 15mmol) in anhydrous acetonitrile (10ml) is stirred at 5-10ºC for 2-3min. Then, 1,1,3,3-tetramethyldisiloxane (1.79ml, 10mmol) is added and the mixture is refluxed for 30min. The remaining siloxane products are destroyed by adding 45% hydrofluoric acid (2.0ml) and refluxing for 5min. On completion, the reaction mixture is taken up in dichloromethane (20ml) and washed with water (20ml), 1N $NaHSO_3$(10ml) and water again. Drying (Na_2SO_4) and evaporation of the solvents gives crude cyclohexyl iodide which is purified by Kugelrohr distillation (1.58g, 75%) b.p.: 180-183ºC (lit. b.p.: 179ºC/760torr)[28]. ^{1}H-NMR (CCl_4) δ ppm: 1.41 (m, 6H, CH_2), 1.92 (m, 4H, CH_2-CH), 4.14 (m, 1H, CH).

Typical procedure for Method B. Cyclopentyl iodide.

A solution of 1,1,3,3-tetramethyldisiloxane (2.69ml, 15mmol) in dichloromethane (6ml) is dropwise added to a cooled mixture (-5ºC) of cyclopentanone oxide (0.87ml, 10mmol), iodine (2.03g, 8mmol) and dichloromethane (6ml) . The reaction mixture is stirred at room temperature for 12min. On completion, the mixture is taken up over dichloromethane (30ml) and washed with water (20ml x 2) $NaHCO_3$ (20ml x 2) and $NaHSO_3$(20ml x 2). Drying and evaporation of the solvent yields crude cyclopentyl iodide and siloxane compounds, which is purified by distillation. (1.69g, 90%, b.p.: 143ºC/760torr) (lit. 56-68ºC/20torr)[29]. ^{1}H-NMR ($CDCl_3$) δ ppm : 3.2-1.4 (m, 8H, CH_2), 4.06 (m, 1H, CH).

1-Phenyl-2-bromoethane.

Over a cooled (0ºC) mixture of trifluoroacetic acid (8ml) , lithium bromide (1.02g, 12mmol) and trimethylchlorosilane (1.92ml, 15mmol), epoxystyrene (1.41ml, 10mmol) is added. After the initial exothermic reaction, TMDS (1.79ml, 10mmol) is added, and the suspension is heated at 50ºC for 15h. Then, the remaining solixane products

are destroyed by adding hydrofluoric acid/methanol (2.5N, 20ml) and refluxing the mixture for 5min. The reaction mixture is taken up over dichloromethane (20ml) and washed successively with water (15ml) and saturated sodium hydrogen carbonate solution (15ml x 3). Drying and evaporation of the solvents yields crude 1-phenyl-2-bromoethane, which is purified by Kugelrohr distillation (1.28g, 69%), b.p: 215-220ºC (lit. b.p: 217-218ºC/734 torr)[25a]. ^{1}H-NMR (CCl_4) δ ppm: 2.86 (t, 2H, J= 7Hz, $C\underline{H}_2$-Ar), 4.32 (t, 2H, J= 7Hz, CH_2-Br), 7.10 (s, 5H, arom.).

trans-1-Hydroxy-2-bromocyclohexane.

Over a suspension of lithium bromide (1.0g, 12mmol) and trimethylchlorosilane (1.92ml, 15mmol) in acetonitrile (10ml), 7-oxabicyclo(4.1.0)heptane (cyclohexene oxide) (1.01ml, 10mmol) and 1,1,3,3-tetramethyldisiloxane (1.79ml, 10mmol) are added, and the mixture is refluxed for 7h. After this time, the reaction mixture is trated as above to afford trans-1-hydroxy-2-bromocyclohexane (1.79g, 93%). b.p.: 195-200ºC (lit. b.p.: 88-90ºC/33torr)[28]. ^{1}H-NMR ($CDCl_3$) δ ppm: 1.40 (m, 4H, CH_2), 2.10 (m, 4H, $C\underline{H}_2$-CH), 3.32 (s, 1H, OH), 3.45 (m, 1H, CHBr), 3.64 (m, 1H, C$\underline{H}$--OH).

1,2-Dibromopropane.

A mixture of epoxypropene (0.70ml, 1.0mmol), sodium iodide (2.00g, 13.3mmol) and trimethylchlorosilane (1.92ml, 15mmol) in anhydrous acetonitrile (10ml) is stirred at 5-10ºC for 2-3min. Then , TMDS (1.79ml, 10mmol) is added and the mixture is refluxed for 6h. During this time, the evolved propene is bubbled through a solution of bromine (0.5ml, 10mmol) in dichloromethane (20ml) until decoloration. Evaporation and distillation of this solution affords 1,2-dibromopropane (1.73g, 86%) b.p: 140-142ºC (lit. b.p: 140ºC/760torr)[27] ^{1}H-NMR ($CDCl_3$) δ ppm: 1.71 (d, 3H, CH_3), 3.25-4.32 (m, 3H, CH, CH_2)..

General procedure for the reduction of p-benzoquinones.

A solution of the corresponding p-benzoquinone 7 (10mmol), 1,1,3,3-tetramethyldisiloxane (1.79ml, 10mmol) and iodine (0.05g) in dichloromethane (30ml) is stirred at reflux for 30min. Then , the reaction mixture is extracted with 1N NaOH (30ml), the organic layer is eliminated, and the inorganic one acidified with conc. HCl and extracted with ethyl acetate (10ml x 4). Drying (Na_2SO_4) and evaporation of the solvents yields a fairly pure hydroquinone 8.

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