Bull. Chem. Soc. Jpn., ***69***, *685—691 (1996)*

Oxidation of Organic Compounds with Tetrabutylammonium Periodate in the Presence of Lewis Acids in Aprotic Organic Solvents

Habib Firouzabadi,* Alireza Sardarian, and Hasan Badparva

Chemistry Department, Shiraz University, Shiraz 71454, Iran

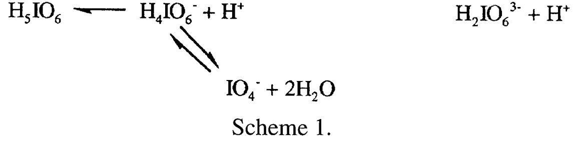
(Received June 14, 1995)

Tetrabutylammonium periodate is able to oxidize alcohols to their carbonyl compounds, α-hydroxy ketones to α-diketones, α-hydroxy carboxylic acids to the carbonyl compounds (accompanied with decarboxylation), thiols to disulfides, thioethers to sulfoxides in $CHCl_3$ and CH_3CN in the presence of $AlCl_3$ and $BF_3 \cdot Et_2O$ as catalysts.

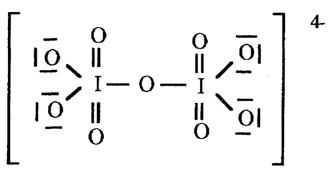
Oxidation of organic substrates in the absence of protons in organic solvents is of importance. This subject has been under intensive investigation in recent years. Along this line, we have introduced potentially useful oxidants in the last decade.[1)]

Recently we have focussed our attention on the Lewis acid assisted reactions in aprotic organic solvents. Highly selective amidation of benzylic alcohols with nitriles in the presence of boron trifluoride,[2)] highly efficient and selective silylation of alcohols in the presence of amines and thiols in the presence of zinc chloride,[3)] and activation of sodium and silver bromates in the presence of Lewis acids for the oxidation of organic compounds[4)] in aprotic organic solvents are our recent achievements.

Periodic acid is a strong oxidant. The standard potential E° for the periodate-iodate couple in acid solution is about 1.6 V; in alkaline solution the value is lower, and the standard potential is equal to 0.7 V.[5)] In aqueous solution (pH = 0—7), periodic acid exists as an equilibrium mixture between the free acid and its various ions. A shift in the equilibrium is expected on dilution or on mixing with an organic solvent (Scheme 1). The aqueous solution of periodic acid is apparently a mixture of mono anionic species.[6)] However, it has been shown that in alkaline aqueous solutions of periodate, a dimeric species is formed (Scheme 2).[7)] Therefore, pH of the media and the nature of the solvent is very important and affect drastically the nature and the structure of the different periodate species present in the reaction media. These, in turn, might affect the oxidation ability and the mode of the reactions by the reagent.



Scheme 1.



Scheme 2.

The application of the periodic acid and periodate salts in organic synthesis has been extensively reviewed.[7)] Reactions proceeded in aqueous media in the presence of protic acids and sometimes in the presence of a series of aprotic solvents miscible with water.[8)]

However, the necessity of employing water as a solvent or a co-solvent mixed with an organic solvent e.g. DMF, and also protic acidic media, puts some restrictions on the use of periodates for the oxidation of acid sensitive and easily hydrolyzed molecules.[9)] To overcome this restriction, quaternary ammonium periodates have been prepared and used for the oxidation of organic compounds under nonaqueous conditions.[10—14)] The solubility of the quaternary ammonium salts in several solvents provide advantages in terms of high reaction rates, low reaction temperatures, and the absence of side reactions.[13)] However, a literature search shows that the synthetic potential of quaternary ammonium periodates, as oxidizing agents, has not been explored properly; e.g. oxidation of hydroxy groups, one of the most encountered functional groups, in organic compounds.

In this study we have found that tetrabutylammonium periodate (TBAPI) is able to oxidize alcohols to the carbonyl compounds, α-hydroxy ketones to α-diketones, α-hydroxy carboxylic acids to carbonyl compounds (accompanied with decarboxylation), thiols to the disulfides and thioethers are also transformed to the sulfoxides without over oxidations in the presence of Lewis acids as catalysts.

Results and Discussion

Tetrabutylammonium periodate (TBAPI)[13—15)] is prepared easily from an aqueous solution of sodium periodate and tetrabutylammonium bromide in a quantitative yield at room

Table 1. Percent Conversion of 4-Methylbenzyl Alcohol with TBAPI in the Presence of Various Lewis Acids in Refluxing CH_3CN[a)]

Lewis acid \ Time/h	1	2	3	4
$ZnCl_2$	0	0	0	0
$SnCl_2\cdot 2H_2O$	0	0	0	0
$NiCl_2$	0	0	0	0
$SnCl_2$	10	20	35	35
$CeCl_3\cdot 7H_2O$	15	35	45	50
$AlCl_3$	70	100		
$BF_3\cdot Et_2O$[b)]	80	100		

a) Alcohol : TBAPI : Lewis Acid = 1 : 0.1 : 0.3. b) *N*-(4-Methylbenzyl)acetamide was also obtained.

Table 2. Percent Conversion of 4-Methylbenzyl Alcohol with TBAPI in the Presence of $AlCl_3$ in Various Solvents

Solvent \ Time/h	1	2	2.5	3	4
Et_2O	—	—	—	—	—
Dichloromethane	—	—	—	—	10
THF	—	—	—	—	30
Toluene	—	—	—	—	60
Chloroform	70	95	—	100	—
Acetonitrile	70	95	—	100	—
1,2-Dichloroethane	75	95	100	—	—

temperature. This oxidizing agent is a white and stable solid compound which could be stored in darkness for months without losing its activity.

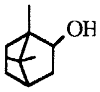
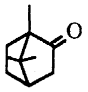
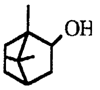
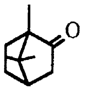
TBAPI is not able to transform hydroxy groups of ordinary alcohols to the corresponding carbonyl compounds in aprotic organic solvents. Oxidations of 4-methylbenzyl alcohol to its corresponding aldehyde with TBAPI in the presence of various Lewis acids: $ZnCl_2$, $SnCl_2\cdot 2H_2O$, $SnCl_4$, $CeCl_3\cdot 7H_2O$, $AlCl_3$, $BF_3\cdot Et_2O$, $NbCl_5$ and $CoCl_2\cdot 6H_2O$ in CH_3CN were examined in the air and under nitrogen atmosphere. The results of the two experimental conditions were more or less the same within the limit of the experimental errors. This observation eliminates the idea of the generation of protic acids by the partial hydrolysis of the catalysts by moisture which in turn could catalyze the reaction. The rate of the reaction was monitored by GLC. Surprisingly, only $AlCl_3$ and $BF_3\cdot Et_2O$ were recognized to be effective catalysts for this purpose (Table 1). The effect of various solvents on the same transformation with TBAPI in the presence of $AlCl_3$ in various solvents, such as Et_2O, CH_2Cl_2, THF, $PhCH_3$, $CHCl_3$, CH_3CN, and $ClCH_2CH_2Cl$, were examined. The rate of the conversion was monitored by GLC. $CHCl_3$, CH_3CN, and $ClCH_2CH_2Cl$ were suitable solvents for this oxidation system (Table 2). The effect of *p*-toluenesulfonic acid as a source of a protic catalyst in the oxidation of the same alcohol in dry CH_3CN with TBAPI was also investigated. The reaction proceeded with lower efficiency even with higher molar ratios of the oxidant in comparison with the amount used in the presence of $AlCl_3$ (0.3 mol). The yield of the generated aldehyde in the mixture did not exceed 50% and various saturated alcohols, under our investigations, remained intact

Table 3. Oxidation of Primary and Secondary Benzylic Alcohols with TBAPI/$AlCl_3$ in Refluxing $CHCl_3$

No.	Substrate	Product	Substrate	Reaction time	Yield	Mp/bp
			/TBAPI/$AlCl_3$	h	%	°C
1	Benzyl alcohol	Benzaldehyde	1 : 0.5 : 0.3	2.5	85	177—178
2	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	1 : 0.5 : 0.3	2.5	80	209—215
3	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	1 : 0.5 : 0.3	2	95	44—47
4	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	1 : 0.5 : 0.3	2	87	248
5	2-Methoxybenzyl alcohol	2-Methoxybenzaldehyde	1 : 0.5 : 0.3	2	80	37—39
6	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	1 : 0.5 : 0.3	2	96	82—85
7	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	1 : 0.5 : 0.5	3	85	105—108
8	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	1 : 0.5 : 0	3	0[a)]	—
9	2-Methoxybenyl alcohol	2-Methoxybenzaldehyde	1 : 0.5 : 0	2	0[a)]	—
10	1-Phenylethanol	Acetophenone	1 : 0.5 : 0.3	2	93	—
11	$4\text{-MeC}_6H_4CH(OH)Et$	4-MeC_6H_4COEt	1 : 0.5 : 0.3	2	90	—
12	$4\text{-PhC}_6H_4CH(OH)Me$	4-PhC_6H_4COMe	1 : 0.5 : 0.3	1.5	97	—
13	Diphenylmethanol	Benzophenone	1 : 0.5 : 0.3	2.5	94	48—50
14	1-Phenylethanol	Acetophenone	1 : 0.5 : 0	2	0[a)]	—
15	Diphenylmethanol	Benzophenone	1 : 0.5 : 0	2.5	0[a)]	—

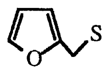
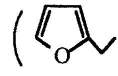
a) Reactions were performed in the absence of $AlCl_3$.

Table 4. Oxidation of Primary and Secondary Saturated Alcohols with TBAPI/$BF_3 \cdot Et_2O$ in Refluxing CH_3CN

No.	Substrate	Product	Substrate/TBAPI/ $BF_3 \cdot Et_2O$	Reaction time h	Yield %	Mp/bp °C
1	$PhCH_2CH_2OH$	$PhCH_2CHO$	1 : 1 : 0.3	4	75	195
2	$PhCH_2CH_2CH_2OH$	$PhCH_2CH_2CHO$	1 : 1 : 0.3	4	70	97—98 12 mmHgd)
3	$(PhCH_2)_2CHOH$	$(PhCH_2)_2CO$	1 : 1 : 0.3	4	60	32—34
4	Cyclohexanol	Cyclohexanone	1 : 1 : 0.3	4	65a)	155
5	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	1 : 1 : 0.3	4	70a)	135
6	$CH_3(CH_2)_5CHOHCH_3$	$CH_3(CH_2)_5COCH_3$	1 : 1 : 0.3	4	65a)	149—150
7	$CH_3(CH_2)_{10}CH_2OH$	$CH_3(CH_2)_{10}CHO$	1 : 1 : 0.3	4	73a)	185 100 mmHgd)
8			1 : 1 : 0.3	4	80a)	175—177
9	$PhCH_2CH_2OH$	$PhCH_2CHO$	1 : 1 : 0.3	4	0b)	195
10			1 : 1 : 0.3	4	0b)	—
11	$PhCH_2CH_2OH$	$PhCH_2CHO$	1 : 1 : 0	4	0c)	—
12	$Ph(CH_2)_2CH_2OH$	$Ph(CH_2)_2CHO$	1 : 1 : 0	4	0c)	—

a) GC yield. b) With $AlCl_3$ as catalyst. c) Without catalyst. d) 1 mmHg = 133.322 Pa.

Table 5. Oxidation of Thiols with TBAPI/$AlCl_3$ in $CHCl_3$ at Room Temperature

No.	Substrate	Product	Reaction time min	Yielda) %	Mp/bp °C	
1	Benzenethiol	Diphenyl disulfide	10	98	59—60	
2	Phenylmethanethiol	Dibenzyl disulfide	10	100	68—69	
3	3-Methylbenzenethiol	Di-*m*-tolyl disulfide	12	95	45	
4	Cyclohexanethiol	Dicyclohexyl disulfide	8	95	125—130	
5	*n*-C_4H_9SH	(*n*-$C_4H_9S)_2$	10	90	229—233	
6	*n*-$C_{12}H_{25}SH$	(*n*-$C_{12}H_{25}S)_2$	13	97	—	
7			10	98	112—115	0.5 mmHg
8	Benzenethiol	Diphenyl disulfide	10	Traceb)		
9	Phenylmethanethiol	Dibenzyl disulfide	10	Traceb)	—	

a) Substrate/TBPI/$AlCl_3$ (1 : 0.3 : 0.2). b) Without catalyst.

Table 6. Oxidation of Sulfides with TBAPI/$AlCl_3$ in Refluxing CH_3CN to Sulfoxides

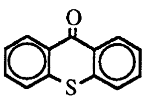
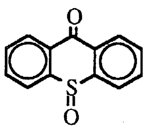
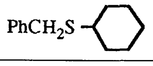
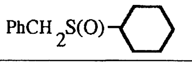
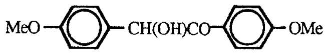
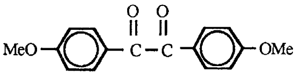
No.	Substrate	Product	Reaction time h	Yield %	Mp/bp °C	
1	PhSMe	PhS(O)Me	4	70	139—141	14 mmHg
2	$PhCH_2SC_4H_9$	$PhCH_2S(O)C_4H_9$	4	75	62—64	
3	$(PhCH_2)_2S$	$(PhCH_2)_2SO$	4	75	134—136	
4	$PhCH_2SPh$	$PhCH_2S(O)Ph$	6	75	123—124	
5			8	65	—	
6	4-$NO_2C_6H_4SPh$	4-$NO_2C_6H_4S(O)Ph$	10	60	—	
7			5	73	—	

Table 7. Miscellaneous Oxidations with TBAPI/$AlCl_3$ in Refluxing $CHCl_3$

No.	Substrate	Product	Reaction time	Yield[a)]	Mp/bp
			h	%	°C
1	PhCH(OH)COPh	PhCOCOPh	2.5	85	94—95
2			3	70	132—134
3	$PhCH(OH)CO_2H$	PhCHO	2	90	177—178
4	$Ph_2C(OH)CO_2H$	Ph_2CO	2	70	49—51
5	PhCH(OH)CH(OH)Ph	PhCOCOPh	3	70	94—95
		PhCHO		22	177—178
6	$HOCH_2CH(OH)Ph$	PhCHO	2.5	100	177—178

a) Substrate/TBAPI/$AlCl_3$ (1 : 0.3 : 0.2).

Table 8. Comparision of the Results Obtained with TBAPI/Lewis Acid Oxidations with the Other Reported Methods

Entry No.	Substrate	Product	TBAPI	$BaMnO_4$[1a)]	$Ba(MnO_4)_2$[1e)]	$Zn(BiO_3)_2$[1f)]
			Lewis acid yield (h)	Yield (h)	Yield (h)	Yield (h)
1	Benzyl alcohol	Benzaldehyde	85 (2.5)	90 (1.5)	90 (0.4)	95 (0.3)
2	Diphenylmethanol	Benzophenone	94 (2.5)	100 (0.5)	99 (1)	100 (0.3)
3	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	85 (3)	60 (4.5)	90 (0.5)	90 (3)
4	Benzoin	Benzil	85 (2.5)	—	96 (0.25)	97 (0.7)
5	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	95 (2)	—	—	93 (2)
6	Benzilic acid	Benzophenone	70 (2)	—	95 (1.5)	95 (0.5)
7	2-Phenylethanol	2-Phenylacetaldehyde	75 (4)	—	—	90 (1.5)
8	Cyclohexanol	Cyclohexanone	65 (4)	60 (2.25)	60 (2.25)	70 (24)
9	1-Phenylethanol	Acetophenone	93 (2)	—	94 (0.25)	90 (2)
10	Benzenethiol	Diphenyl disulfide	98 (0.12)	—	—	97 (0.25)
11	Phenylmethanethiol	Dibenzyl disulfide	100 (0.12)	—	—	93 (0.2)
12	Cyclohexanethiol	Dicyclohexyl disulfide	95 (0.1)	—	—	99 (0.25)
13	PhSMe	$Ph\overset{O}{\overset{\Vert}{S}}Me$	70 (4)	—	—	78 (0.3)
14	$PhSCH_2Ph$	$Ph\overset{O}{\overset{\Vert}{S}}CH_2Ph$	75 (6)	—	88(4)	75 (1.25)
15	$PhCH_2S(CH_2)_3CH_3$	$PhCH_2\overset{O}{\overset{\Vert}{S}}(CH_2)_3CH_3$	75 (4)	—	70 (5)	70 (0.8)

under the same reaction conditions. Therefore, we recognized that *p*-toluenesulfonic acid was not a suitable catalyst for the oxidation with TBAPI.

Development of a yellow color between $AlCl_3$ and TBAPI, in the reaction mixture, indicates the formation of a complex which may act as a new oxidizing moiety in the mixture. The color was changed from yellow to white as the reaction proceeded to completion. Trifluoroborane behaves differently and such color development was not observed in the reaction mixture.

For comparison, we have also investigated the oxidation of 4-methylbenzyl alcohol in aqueous organic-solvent mixtures e.g. H_2O/EtOH/HOAC and H_2O/acetone/HOAC, in the presence of KIO_4. The oxidant worked only under reflux conditions. In the former solvent mixture, the corresponding carboxylic acid, aldehyde, and several other unidentified products were formed. In the latter solvent mixture, the corresponding carboxylic acid was isolated as the sole product from the mixture. Saturated alcohols in both solvent mixtures remained intact.

Oxidation of benzylic alcohols to their corresponding carbonyl compounds was performed successfully in $CHCl_3$ in the presence of $AlCl_3$ with TBAPI (Table 1). The same reactions, in the presence of $BF_3{\cdot}Et_2O$ in CH_3CN produced acetamides of the corresponding alcohols in high yields.[3)] Primary and secondary nonbenzylic alcohols were transformed to their carbonyl compounds in the presence of $BF_3{\cdot}Et_2O$ in CH_3CN (Table 4). Surprisingly, the same transformations did not proceed in the presence of $AlCl_3$ under similar conditions. Allylic alcohols are not oxidized with this reagent in the presence of the catalysts.

The mildness of the reagent has been shown by the facile oxidation of thiols to the disulfides in $CHCl_3$. Both $AlCl_3$ and $BF_3{\cdot}Et_2O$ catalyzed the reactions, but $AlCl_3$ was a more effective catalyst for this transformation (Table 5). Conversion of sulfides to the sulfoxides, which are important synthetic precursors, could be achieved by many reagents which are available in the literature.[1f,16)] TBAPI in boiling $CHCl_3$ is also reported[13)] to be an effective oxidant for the oxidation of sulfides to their sulfoxides. We have used this method for the oxidation of the substrates under our investigation. Overoxidized products were isolated from the reaction mixture without exception. This reagent in CH_3CN in the presence of $AlCl_3$ converted sulfides to the sulfoxides without further oxidation (Table 6). $BF_3\cdot Et_2O$ was ineffective for this purpose.

α-Hydroxy ketones and α-hydroxy carboxylic acids in the presence of $AlCl_3$ in $CHCl_3$ were converted to the α-diketones and decarboxylated carbonyl compounds with TBAPI in good yields. With the same catalyst, 1,2-diphenyl-1,2-ethanediol produced benzil and benzaldehyde in 70 and 22% yields, respectively. 1-phenyl-1,2-ethanediol yielded benzaldehyde quantitatively in $CHCl_3$ (Table 7). We have compared the results of our investigations with barium manganate, $BaMnO_4$ a commercially available reagent,[1a] barium permanganate, $Ba(MnO_4)_2$[1e] and zinc bismuthate, $Zn(BiO_3)_2$[1f] the two recently reported reagents. The results show that TBAPI is as effective as the above mentioned oxidants. TBAPI is superior to $BaMnO_4$ which has not been able to oxidize sulfides to their sulfoxides (Table 8).

Experimental

General. All yields refer to isolated products, unless otherwise stated. All oxidation products were characterized by comparison of their spectral and physical data with the authentic samples. Melting points were determined in open capillaries with a Galen Kamp Melting Point Apparatus. Infrared (IR) spectra were obtained using a Perkin–Elmer IR 781 spectrophotometer. ^{1}H NMR spectra were run on a Hitachi, R-2413, 60 MHz NMR spectrometer. Purity of the substrates were accomplished by TLC on silica gel polygram SIL/UV 254 plates or on GLC on a Shimadzu Model GC-14A, instrument with a hydrogen flame ionization detector and equipped with a column of 5% SE-30 Shimalite W (60—80 mesh). Chemicals were either prepared in our laboratories or were purchased from Fluka, Merck, or BDH Chemical Companies.

Anhydrous solvents were generally prepared by drying over molecular sieves 4 Å, or $CaCl_2$.

General Procedure for the Oxidation of Benzylic Alcohols to the Corresponding Carbonyl Compounds with TBAPI in the Presence of $AlCl_3$. In a round-bottomed flask (50 ml), equipped with a condenser and a magnetic stirrer, a solution of alcohol (1 mmol) in chloroform (10—20 ml) was prepared. TBAPI (0.5—1 mmol) and $AlCl_3$ (0.3—0.5 mmol) were added to the solution and the reaction mixture was stirred under reflux condition for 2—4 h. The progress of the reaction was followed by TLC (eluent: CCl_4/Et_2O). The reaction mixture was filtered and the solid material was washed with ether several times (3×15 ml). The filtrates were combined together and evaporated on a rotary evaporator. The residue was redissolved in ether (20 ml) and the resulting brown solution was treated with sodium thiosulfate (20%, 20 ml) in order to reduce the produced iodine. The aqueous layer was separated, and the ethereal solution was extracted with water (2×20 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on a silica-gel plate or a silica-gel column with appropriate eluent to afford pure products in 80—96% yields (Table 3).

Oxidation of 4-Methylbenzyl Alcohol to 4-Methylbenzaldehyde as a Typical Procedure for Conversion of Primary Benzylic Alcohols to the Corresponding Aldehydes with TBAPI in the Presence of $AlCl_3$. To a solution of 4-methylbenzyl alcohol (0.12 g, 1 mmol) in chloroform (10 ml) in a 50 ml round-bottomed flask equipped with a condenser, TBAPI (0.212 g, 0.5 mmol) and $AlCl_3$ (0.04 g, 0.3 mmol) were added. The reaction mixture was stirred magnetically under reflux condition for 2 h. The progress of the reaction was monitored by TLC (eluent: CCl_4/Et_2O: 4/1). The reaction mixture was filtered and the solid material was washed with ether several times (3×15 ml). The combined filtrates were evaporated on a rotary evaporator and the residue was redissolved in ether (20 ml). The ethereal solution was treated with 20% aqueous sodium thiosulfate solution (20 ml) in order to reduce the produced iodine. The aqueous layer was separated and the organic layer was extracted with water (2×20 ml). The organic layer was separated and dried over anhydrous $MgSO_4$ and the resulting crude material was purified on a silica-gel plate (eluent: CCl_4/Et_2O: 4/1). Pure 4-methylbenzaldehyde was obtained, yield 0.115 g, 96% (Table 3).

Oxidation of Diphenylmethanol to Benzophenone as a Typical Procedure for the Conversion of Secondary Benzylic Alcohols to the Corresponding Ketones with TBAPI in the Presence of $AlCl_3$. In a round-bottomed flask (50 ml) equipped with a condenser and a magnetic stirrer, a solution of diphenylmethanol (0.184 g, 1 mmol) in chloroform (15 ml) was prepared. TBAPI (0.21 g, 0.5 mmol) and $AlCl_3$ (0.04 g, 0.3 mmol) were added and the reaction mixture was stirred under reflux condition for 2.5 h. The progress of the reaction was monitored by TLC (eluent: CCl_4/Et_2O: 3/1). The reaction mixture was filtered and the solid material was washed with ether several times (3×15 ml). The combined filtrates were evaporated on a rotary evaporator. The resulting crude material was redissolved in ether (20 ml) and treated with sodium thiosulfate (20%, 20 ml) in order to reduce the produced iodine. The aqueous layer was separated and the ethereal solution was extracted with water (2×20 ml). The organic layer was dried over anhydrous $MgSO_4$, and was evaporated. The residue was chromatographed on a silica-gel plate to afford pure benzophenone, yield 0.172 g, 94%, mp 49 °C, lit,[17] 49—51 °C (Table 3).

General Procedure for the Oxidation of Saturated Alcohols to the Corresponding Carbonyl Compounds with TBAPI in Presence of BF_3/Et_2O. In a round-bottomed flask (50 ml) equipped with a condenser, a solution of alcohol (1 mmol) in acetonitrile (10 ml) was prepared. TBAPI (1 mmol) and BF_3/Et_2O (0.1 ml, 0.3 mmol) were added to the solution. The mixture was stirred under reflux condition for 4—5 h. The progress of the reaction was monitored by GLC or TLC. The reaction mixture was filtered from a short pad of silica gel (Type 60, Merck), and the filter cake was washed with carbon tetrachloride (30 ml). The combined filtrates were evaporated and the residue was redissolved in ether (20 ml). The ethereal solution was treated with 20% aqueous solution of sodium thiosulfate (20 ml) in order to reduce the produced iodine. The aqueous layer was separated and the ethereal phase was extracted with water (2×20 ml). The organic layer was separated and was dried over anhydrous $MgSO_4$. The solvent was evaporated and the resulting crude material was purified by column chromatography on silica gel (eluent: CCl_4/Et_2O: 5/1) to afford pure products, yields 60—75% (Table 4).

Oxidation of 2-Phenylethanol to 2-Phenylacetaldehyde as a Typical Procedure for the Oxidation of Primary Saturated Alcohols to the Corresponding Aldehydes with TBAPI in the Presence of BF_3/Et_2O. To a solution of 2-phenylethanol (0.12 g, 1 mmol) in acetonitrile (10 ml), TBAPI (0.434 g, 1 mmol) and BF_3/Et_2O (0.1 ml, 0.3 mmol) were added and the mixture was refluxed for 4 h. The reaction progress was followed by TLC (eluent: CCl_4/Et_2O: 5/1). The reaction mixture was filtered from a short pad of silica gel (Type 60, Merck). The filter cake was washed with carbon tetrachloride several times (3×15 ml). The combined filtrates were evaporated and the resulting crude material was redissolved in ether (20 ml). Work-up was performed as mentioned in the general procedure and pure 2-phenylacetaldehyde was obtained, yield 0.092 g, 75% (Table 4).

General Procedure for the Oxidation of Thiols to the Corresponding Disulfides with TBAPI in the Presence of $AlCl_3$. In a round-bottomed flask (25 ml) equipped with a magnetic stirrer, a solution of thiol (1 mmol) in chloroform (5 ml) was prepared. TBAPI (0.3 mmol) and $AlCl_3$ (0.2 mmol) were added to the solution and the mixture was stirred at room temperature for 5—10 min. The progress of the reaction was monitored by TLC (eluent: CCl_4/ether: 8/1—4/1). The reaction mixture was filtered from a short pad of silica gel (Type 60, Merck) and the filter cake was washed with ether several times (2×20 ml). The filtrate was evaporated, and the crude disulfide was purified in the following way: The crude material was redissolved in ether (20 ml) and the reddish brown solution was treated with sodium thiosulfate (20%, 10 ml) in order to reduce the produced iodine. The aqueous layer was separated and the organic layer was extracted with water (2×20 ml). The solvent of the organic layer after drying over $MgSO_4$ was evaporated and the resulting crude product was purified on a silica-gel plate (eluent: CCl_4/Et_2O 8/1—4/1). Pure disulfides were obtained, yields 90—100% (Table 5).

Oxidation of Phenylmethanethiol to Dibenzyl Disulfide as a Typical Procedure for the Conversion of Thiols to the Corresponding Disulfides with TBAPI in the Presence of $AlCl_3$. To a solution of phenylmethanethiol (0.124 g, 1 mmol) in chloroform (5 ml) in a round-bottomed flask (25 ml) equipped with a magnetic stirrer, TBAPI (0.145 g, 0.3 mmol) and $AlCl_3$ (0.027 g, 0.2 mmol) were added. The reaction mixture was stirred magnetically at room temperature for 5 min. The progress of the reaction was followed by TLC (eluent: CCl_4/ether: 8/1). The reaction mixture was filtered through a short pad of silica gel (2 g, Type 60, Merck), and the filter cake was washed with ether (30 ml). The filtrate was evaporated and the resulting crude material was redissolved in ether (20 ml). The work-up was performed as mentioned in the general procedure. Pure dibenzyl disulfide was obtained, yield 0.122 g, 100%, mp 67 °C, lit,(17) 68—69 °C (Table 5).

General Procedure for the Oxidation of Sulfides to the Corresponding Sulfoxides with TBAPI in the Presence of $AlCl_3$. In a round-bottomed flask (50 ml) equipped with a condenser and a magnetic stirrer, a solution of sulfide (1 mmol) in acetonitrile (10—20 ml) was prepared. TBAPI (1 mmol) and $AlCl_3$ (0.2—0.5 mmol) were added to the solution and the reaction mixture was stirred magnetically under reflux condition for 6—10 h. The progress of the reaction was followed by TLC (eluent: CCl_4/ether). The reaction mixture was filtered and the solid residue was washed with carbon tetrachloride (20 ml). The filtrates were combined together, evaporated on a rotary evaporator, and the residue was redissolved in ether (20 ml). The resulting solution was treated with sodium thiosulfate solution (20%, 20 ml) in order to reduce the produced iodine. The aqueous layer was separated and the ethereal phase was washed with water. The organic layer was separated and was dried over $MgSO_4$. Evaporation of the solvent resulted in crude material which was purified on a silica-gel plate or silica-gel column with an appropriate eluent. The pure products were obtained, yields 60—75% (Table 6).

Oxidation of Benzyl Phenyl Sulfide, A Typical Procedure for the Conversion of Sulfides to Sulfoxides with TBAPI in the Presence of $AlCl_3$. A solution of benzyl phenyl sulfide (0.2 g, 1 mmol) in acetonitrile (10 ml) in a round-bottomed flask (25 ml) was prepared. To the resulting solution, the oxidant (0.43 g, 1 mmol) and $AlCl_3$ (0.2 mmol) were added and the reaction mixture was stirred magnetically under reflux condition for 6 h. The progress of the reaction was followed by TLC (eluent: CCl_4/Et_2O: 4/1). The reaction mixture was filtered and the solid material was washed with carbon tetrachloride (30 ml). Work-up was performed as mentioned in the general procedure and pure sulfoxide was obtained, yield 0.163 g, 75%, mp 120—123 °C, lit,(17) 121—125 °C (Table 6).

Conclusion

In this study we have introduced a new oxidation method for useful functional group transformations with tetrabutylammonium periodate (TBAPI) in the presence of $AlCl_3$ and $BF_3 \cdot Et_2O$ as catalysts and in aprotic organic solvents. This method has not been reported previously in the literature. We have shown the effects of Lewis acids and the solvents upon the selectivity and the reactivity of the reagent. Work-up of the reaction mixture is easy and not time-consuming. Yields of the products were reasonable and the reaction conditions were rather mild. Our new modification for the oxidations with TBAPI has expanded the spectrum of the application of this commercially available oxidizing agent in organic synthesis and is also a useful addition to the present methodologies.

The authors are thankful to Shiraz University Research Council for the partial support of this work and N. Farah and Z. Pakniyat for typing the manuscript.

References

1) a) H. Firouzabadi and Z. Mostafavipoor, *Bull. Chem. Soc. Jpn.*, **56**, 914 (1983); b) H. Firouzabadi, A. Sardarian, M. Naderi, and B. Vessal, *Tetrahedron*, **40**, 5001 (1984); c) H. Firouzabadi, N. Iranpoor, F. Kiaeezadeh, and J. Toofan, *Tetrahedron*, **42**, 719 (1986); d) H. Firouzabadi, D. Mohajer, and M. Entezari-Moghaddam, *Synth. Commun.*, **16**, 723 (1986); e) H. Firouzabadi, E. Mottaghinejad, and M. Seddighi, *Synthesis*, **1989**, 376; f) H. Firouzabadi and I. Mohammadpoor-Baltourk, *Bull. Chem. Soc. Jpn.*, **65**, 1131 (1992); g) B. Tamami, H. Firouzabadi, M. M. Lakouraj, and A. R. Mahdavian, *Iranian J. Polym. Technol.*, **3**, 82 (1994).

2) H. Firouzabadi, A. Sardarian, and H. Badparva, *Synth. Commun.*, **24**, 601 (1994).

3) H. Firouzabadi and B. Karimi, *Synth. Commun.*, **23**, 1633 (1993).

4) H. Firouzabadi and I. Mohammadpoor-Baltourk, *Bull. Chem. Soc. Jpn.*, **68**, 2319 (1995).

5) W. H. Latimer, "Oxidation Potentials," 2nd ed, Prentice Hall, London (1952), pp. 66—67.

6) C. E. Crouthamel, A. M. Hayes, and D. S. Martin, *J. Am. Chem. Soc.*, **73**, 82 (1951).

7) G. J. Buist, W. C. P. Hipperson, and J. D. Lewis, *J. Chem. Soc. A*, **1969**, 307.

8) A. Fatiadi, *Synthesis*, **1974**, 229.

9) H. O. House, "Modern Synthetic Reactions," 2nd ed, Benjamin, New York (1972).

10) A. K. Oureshi and B. Sklarz, *J. Chem. Soc. C*, **1966**, 412.

11) G. E. Keck and S. A. Fleming, *Tetrahedron Lett.*, **1978**, 4763.

12) K. Inomata, Y. Nakayama, and H. Kotake, *Bull. Chem. Soc. Jpn.*, **53**, 565 (1980).

13) E. Santaniello, A. Manzocchi, and C. Farachi, *Synthesis*, **1980**, 563.
14) E. Santaniello, F. Ponti, and A. Manzocchi, *Tetrahedron Lett.*, **1980**, 2655.
15) P. Ferraboschi, M. S. Azadani, E. Santaniello, and S. Trave, *Synth. Commun.*, **16**, 43 (1986).
16) M. Hirano, H. Kudo, and T. Morimoto, *Bull. Chem. Soc. Jpn.*, **65**, 1744 (1992).
17) Aldrich Catalog Handbook of Fine Chemicals, 1990—91.