Hypervalent Iodine Oxidation of Silyl Enol Ethers. A Direct Route to α-Hydroxy Ketones

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Hypervalent iodine oxidation of various silyl enol ethers (aromatic, heteroaromatic, and aliphatic) using iodosobenzene–boron trifluoride diethyl ether–water provides a general and direct route for the α-hydroxylation of ketones. The structures of 2-hydroxy- (**8**) and 3-hydroxy-acetylpyridine (**9**) are discussed as well as the scope and mechanism of the reaction.

There has been considerable recent interest in the development of direct methods for the synthesis of α-hydroxy ketones [1] which are important intermediates in organic synthesis. Our initially discovered method for the α-hydroxylation of ketones using iodobenzene diacetate–potassium hydroxide–methanol provides an efficient route to α-hydroxy ketone dimethyl acetals.[2] Hydrolysis of the dimethyl acetal yields the α-hydroxy ketone (Scheme 1).

$$RC(O)Me \longrightarrow RC(OMe)_2CH_2OH \longrightarrow RC(O)CH_2OH$$

Scheme 1.

Although the above procedure is quite general for the synthesis of α-hydroxy ketone dimethyl acetals,[2d] hydrolysis of the acetal to the ketone is frequently problematic. In view of this limitation we recently developed another direct route based on hypervalent iodine to produce hydroxymethyl aryl ketones.[3] Following this method, silyl enol ethers of acetophenones and acetylpyridines were oxidized to the corresponding α-hydroxy ketones using the system iodosobenzene–boron trifluoride–diethyl ether–water in dichloromethane at −40 °C[3] (Scheme 2).

$$ArC(OSiMe_3)=CH_2 \xrightarrow{i} ArC(O)CH_2OH$$
$$Ar = C_6H_5, p\text{-}OMeC_6H_4, p\text{-}ClC_6H_4, 2\text{-pyridyl}, 3\text{-pyridyl}$$

Scheme 2. *Reagents and conditions:* i, $PhIO–BF_3{\cdot}Et_2O–H_2O$, CH_2Cl_2, −40 °C

However, these conditions were not successful for the α-hydroxylation of aliphatic ketones, propiophenone, and several heterocyclic ketones (*e.g.* 2-acetylfuran). α-Hydroxy ketones were formed in poor yields and the major products in these cases were mixtures of the starting ketone and the 1,4-diketone (coupling product).[4] It is impractical to increase the amount of iodosobenzene because of its limited solubility in dichloromethane or diethyl ether. We found however that use of a large excess of water in the absence of an organic solvent brings about the α-hydroxylation of a wide variety of ketones in very high yields. These conditions substantially improved the yields of previously reported α-hydroxy ketones as well.[3] In the present paper we describe our results.

Treatment of various acetophenone silyl enol ethers (**1a**—**d**) with iodosobenzene (1.1 equiv.) and boron trifluoride diethyl ether (2 equiv.) in water at 0—5 °C during 3—4 h afforded the corresponding α-hydroxyacetophenones (**2a**—**d**) in high yields (Table). Similarly propiophenone silyl enol ether (**1e**) also yielded α-hydroxypropiophenone (**2e**) (Scheme 3).

These reaction conditions were successfully applied to various heterocyclic ketone silyl enol ethers namely 2-acetyl- (**3**) and 3-acetyl-pyridines (**4**), 2-acetylfuran (**5**) and 2-acetylbenzofuran

$$\underset{(1)}{XC_6H_4{-}C(OSiMe_3){=}CHR'} \xrightarrow{i} \underset{(2)}{XC_6H_4{-}C(O)C(OH)HR'} + PhI$$

	X	R′
a;	H	H
b;	PMe	H
c;	Cl	H
d;	NO_2	H
e;	H	Me

Scheme 3. *Reagent:* i, $PhIO–BF_3{\cdot}Et_2O–H_2O$

(**7**). The α-hydroxy ketones (**8**)—(**10**) and (**12**) were obtained in very good yield (Table 1). Oxidation of 2-acetylthiophene silyl enol ether (**6**) gave an unacceptable yield (10%) of the 2-hydroxyacetylthiophene (**11**) under the standard conditions. The major product formed in this reaction was 1,4-di(2′-thienyl)butane-1,4-dione. Therefore, we increased the amount of water and reaction time in order to achieve maximum hydroxylation of (**6**). Accordingly, oxidation of (**6**) using excess water (2 × more than in the standard conditions) and a reaction time of 2 days, afforded (**11**) in 50% yield (Scheme 4).

$$\underset{\begin{array}{c}(3)\ 2\text{-Isomer}\\(4)\ 3\text{-Isomer}\end{array}}{Pyridyl{-}C(=CH_2)OSiMe_3} \xrightarrow{i} \underset{\begin{array}{c}(8)\ 2\text{-Isomer}\\(9)\ 3\text{-Isomer}\end{array}}{Pyridyl{-}C(O)CH_2OH}$$

$$\underset{\begin{array}{c}(5)\ Y = O\\(6)\ Y = S\end{array}}{C_4H_3Y{-}C(=CH_2)OSiMe_3} \xrightarrow{i} \underset{\begin{array}{c}(10)\ Y = O\\(11)\ Y = S\end{array}}{C_4H_3Y{-}C(O)CH_2OH}$$

$$\underset{(7)}{Benzofuran\text{-}2\text{-}yl{-}C(=CH_2)OSiMe_3} \xrightarrow{i} \underset{(12)}{Benzofuran\text{-}2\text{-}yl{-}C(O)CH_2OH}$$

Scheme 4. *Reagent:* i, $PhIO–BF_3{\cdot}Et_2O–H_2O$

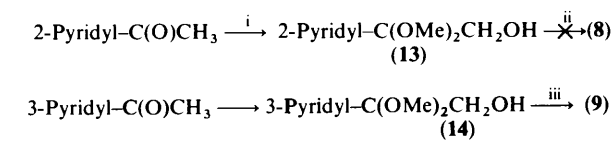
It should be noted that synthesis of 2-hydroxyacetylpyridine (**8**)[5] and 3-hydroxyacetylpyridine (**9**)[6] has been previously reported in the reaction of the appropriate diazo-ketones with aqueous acetic acid (Scheme 5). However, the melting points of the products [(**8**), m.p. 160 °C[5] and (**9**) m.p. 41—42 °C[6]], recorded in these papers do not correspond to the melting points of our products (**8**) m.p. 70—71 °C and (**9**) 112—113 °C, although during the course of this study a confirmatory report on (**8**) m.p. 68—70 °C, appeared (*vide infra*).[7]

$$Pyridyl{-}C(O)CHN_2 \xrightarrow{aq.\ AcOH} \underset{(8),\ (9)}{Pyridyl{-}C(O)CH_2OH}$$

Scheme 5.

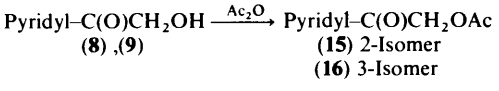
Therefore we decided to synthesize (**8**) and (**9**) according to our previous method as expressed in Scheme 1.[2] This method

gave the dimethyl acetals (**13**) and (**14**) in good yields;[8] hydrolysis of the latter with 6M-hydrochloric acid afforded the pyridine (**9**) (70%). The melting point, mixed melting point, and spectral properties of (**9**) obtained by this approach were identical with those found for the product synthesized by the present approach. Hydrolysis of the dimethyl acetal (**13**) under the same conditions gave unchanged starting acetal (Scheme 6). The use



Scheme 6. *Reagents:* i, $PhIO(OAc)_2$, KOH–MeOH; ii, H^+; iii, HCl

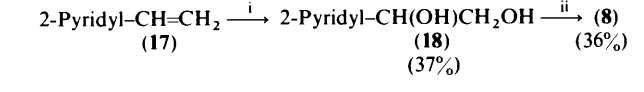
of acetic, concentrated hydrochloric, or hydriodic acid under a wide variety of conditions also gave either the starting material or decomposition products. Although this observation did not help us in preparing the pyridine (**8**), it reflects the value of the present method for the synthesis of α-hydroxy ketones relative to our previous method,[2] especially in the cases where hydrolysis of α-hydroxy ketone dimethyl acetal fails. Elemental analysis and spectral properties (i.r., ^{1}H-n.m.r., m.s.) support the structures of our products unequivocally. The ^{1}H n.m.r. spectrum of (**8**) showed a singlet at δ 5.13 due to methylene protons (CH_2OH) and a broad peak centered at 3.30 due to an hydroxy proton (determined by D_2O addition). Similarly (**9**) and the other hydroxy ketones (**2a**—**d**) and (**10**)—(**12**) also showed these characteristic peaks in their ^{1}H n.m.r. spectra. Finally the structures of (**8**) and (**9**) were confirmed by the following chemical transformations (**8**) ⟶ (**15**) and (**9**) ⟶ (**16**) (Scheme 7). These acetyl derivatives (**15**)[9] and (**16**)[10] are



Scheme 7.

known in the literature and were characterized by their m.p.s and ^{1}H n.m.r. data.

These results reveal that our products (**8**) and (**9**) have the correct structure and that the reported compounds must be in error. Furthermore, very recently, whilst our initial results[3] were in the process of publication, Klayman *et al.*[7] reported the synthesis of (**8**). Their approach involves the oxidation of 2-vinylpyridine (**17**) with potassium permanganate, and selective oxidation of the resulting diol (**18**) with bromine–sodium hydrogen carbonate to form (**8**). The melting point and spectral properties of their product (**8**) are in complete agreement with our data. However, the overall yield (13%) of (**8**) from their method is lower than our present approach (overall yield 55% with respect to ketone). This is another advantage of the present method.



Scheme 8. *Reagents:* i, $KMnO_4$; ii, $Br_2/NaHCO_3$

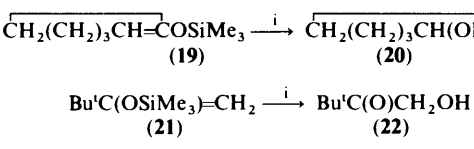
The silyl enol ethers of aliphatic ketones, namely, cyclohexanone (**19**) and pinacolone (**21**) also underwent smooth conversion into the α-hydroxy ketones (**20**) and (**22**) respectively in excellent yields (see Table, Scheme 9).

The pathway which we favour for the general reaction involves formation of intermediate (**23**) which is the synthetic equivalent of the carbonium ion (**24**). Nucleophilic attack of water on (**23**) leads to the α-hydroxy ketone. This sequence may

Table. α-Hydroxy ketones prepared by hypervalent iodine oxidation of silyl enol ethers

Compd.	% Yield[a]	M.p. (°C)	Molecular formula or lit., m.p. (°C) [or b.p. (°C)] ref.
(**2a**)	65	86—87	8.5—86[d]
(**2b**)	72	105—106	104[e], 105—106[f]
(**2c**)	68	121—122	122—123[g]
(**2d**)	70	121	121[h]
(**2e**)	74	Yellow oil[c]	*i*
(**8**)	62	70—71	$C_7H_7NO_2$[j]
(**9**)	54	112—113	$C_7H_7NO_2$[j]
(**10**)	78	82—83	81—82[k]
(**11**)	50[b]	73—74	73—74[l]
(**12**)	59[b]	127—128	128—129[m]
(**20**)	80	Oil[c] (monomer)	149—150 (dimer)[n]
(**22**)	83	63—65/25 mmHg	[64/25 mmHg][o]

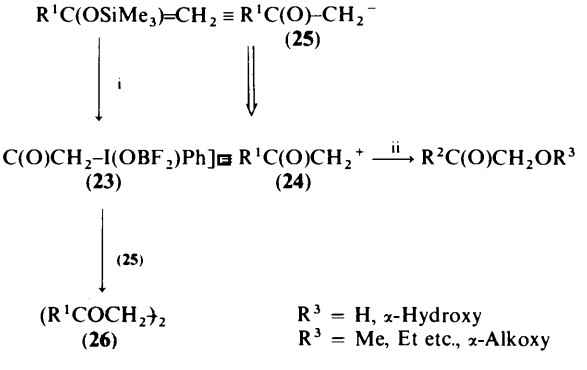
[a] Based on pure recrystallized/distilled product with respect to the amount of silyl enol ether used. [b] Corresponding 1,4-diketone[4] was the minor product (10—20%) which was separated by recrystallization. [c] Separated by column chromatography and characterized by ^{1}H n.m.r. and i.r. spectra. [d] P. Hunaeus and T. Zincke, *Chem. Ber.*, 1877, **10**, 1486. [e] M. Tiffeneau, *Comptes Rendus*, 1910, **150**, 1181. [f] A commercial sample (Aldrich Co.) and our product (**2b**) has same m.p. and mixed m.p. 105—106 °C. [g] W. L. Judefind and E. E. Reid, *J. Am. Chem. Soc.*, 1920, **42**, 1043. [h] C. Engler and O. Zielke, *Chem. Ber.*, 1889, **22**, 203. [i] O. Convert, J. Pinson, and J. Armand, *C.R. Acad. Sci. Ser. C*, 1972, **274**, 296. [j] For analyses and spectral data see the Experimental section. [k] F. Kipnis, H. Solway, and J. Onnfelt, *J. Am. Chem. Soc.*, 1948, **70**, 142. [l] *ibid.*, 1949, **71**, 10. [m] R. B. Wagner and J. M. Tome, *J. Am. Chem. Soc.*, 1950, **72**, 3477. [n] This compound was obtained as a dimer and the properties of the product were identical with a commercial sample (Aldrich Co.). [o] J. P. Guette and N. Spassky, *Bull. Soc. Chim. Fr.*, 1972, 4217; reaction time was 24 h.



Scheme 9. *Reagents:* i, $PhIO–BF_3·Et_2O–H_2O$

be viewed as an umpolung of the carbanion equivalent (**25**). This proposition is supported by our previous results[4] on the carbon–carbon coupling product (**26**) in which the carbanion equivalent (**25**) acts as a nucleophile towards the complex (**23**).

Similarly, formation of α-alkoxy ketones using alcohol instead of water further supports this view (Scheme 10).[11]



Scheme 10. *Reagents:* i, $PhI–OBF_3$; ii, R^2OH

In conclusion, the advantages of the present method are: (*a*) α-hydroxy ketones are obtained in a single step in high yields; (*b*) this method is successful for a wide variety of aromatic, aliphatic and heterocyclic ketones; (*c*) the nitrogen atoms in pyridyl compounds (**8**) and (**9**) or the sulphur atom in thiophene (**11**) are not oxidized under the reaction conditions; (*d*) the process represents a short and efficient synthesis of 2-hydroxy- (**8**) and 3-hydroxy-acetylpyridine (**9**) which are important intermediates for the synthesis of the corresponding oxime methiodides and thiosemicarbazones[7] which are useful as acetylcholinesterase reactivators and antimalarial reagents respectively.* The primary and secondary hydroxy groups of the various α-hydroxy ketones are not oxidized to aldehydes or ketones under the reaction conditions.[12]

Experimental

M.p.s were determined using a Thomas capillary melting point apparatus and are uncorrected. The i.r. spectra were obtained using a Unicam SP1000 i.r. spectrophotometer and peak positions are expressed in cm^{-1}. ^1H N.m.r. spectra were recorded at 60 MHz with a Varian A60 or EM-360 spectrometer using TMS as an internal standard. Mass spectra were scanned with Hewlett Packard GC/MS 5985 apparatus. Unless otherwise stated all α-hydroxy ketones were prepared according to general procedure described.

Starting Materials.—All ketones, iodobenzene, chlorotrimethylsilane and triethylamine were obtained from Aldrich Co. Fresh boron trifluoride–diethyl ether (Aldrich) was used. All solvents were dried and distilled before use.

Iodosobenzene was prepared by oxidation of iodobenzene with 35% peracetic acid (Spectrum Chemical Mfg. Corp.) followed by hydrolysis with aqueous sodium hydroxide.[13]

Silyl enol ethers. Silyl enol ethers prepared from the ketones according to the General Method A of House *et al.*[14] were purified by distillation before use. However, dilute hydrochloric acid was not used in the work up because acid hydrolysis of the silyl enol ethers occurred to a significant extent in some cases.

General Procedure for the Preparation of the α-Hydroxyacetophenones.—Boron trifluoride–diethyl ether (2.84 g, 20 mmol) and then the silyl enol ether (10 mmol) were added to a stirred and ice-cooled (0—5 °C) suspension of iodosobenzene (2.42 g, 11 mmol) in water (50 ml). The mixture was stirred for 2 h, after which the temperature was raised to room temperature; stirring was then continued for a further 2 h, during this time all of the iodosobenzene went into solution indicating completion of the reaction. The solution was neutralized with an excess of solid sodium hydrogen carbonate and then extracted with dichloromethane (5 × 50 ml). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to yield the crude product which contained iodobenzene as a major impurity. Final purification was by column chromatography, distillation, or crystallization. In the cases of solid products addition of hexane generally removed iodobenzene and the crystalline solid separated out of the solution (Table 1).

2-*Hydroxyacetylpyridine* (**8**).—A pure colourless crystalline product (62%) m.p. 70—71 °C (lit.,[9] 68—70 °C) was obtained by addition of mixture of hexane and diethyl ether (20 ml each) to the crude product, followed by filtration and cooling of the filtrate at 0 °C. (Found: C, 61.1; H, 5.2; N, 10.15. Calc. for $C_7H_7NO_2$: C, 61.31; H, 5.15; N, 10.22%); M.s. (70 eV); *m/z* 137 (M^+, 40%), 107 (88), 106 (35), 79 (95), and 78 (100). $\nu_{max.}$(Nujol) 1 720 (C=O) and 3 510 cm^{-1} (OH); δ($CDCl_3$) 3.30 (1 H, br, OH; disappears with D_2O), 5.13 (2 H, s, CH_2OH), and 7.30—8.72 (4 H, m, pyridine).

3-*Hydroxyacetylpyridine* (**9**).—A pure colourless crystalline product (54%), m.p. 112—113 °C was isolated as described for compound (**8**) (Found: C, 61.2; H, 5.2; N, 10.1%); M.s. (20 eV): *m/z* 137 (M^+, 5%), 107 (11), 106 (100), 79 (13), 78 (22). $\nu_{max.}$(KBr) 1 715 (C=O) and 3 500 (OH) cm^{-1}; δ($CDCl_3$) 3.45 (1 H, br, OH, disappears with D_2O), 4.95 (2 H, s, CH_2OH), and 7.32—9.10 (4 H, m, pyridine).

Preparation of 3-*Hydroxyacetylpyridine* (**9**) *According to Scheme 1.*—3-*Hydroxyacetylpyridine dimethyl acetal* (**14**). 3-Acetylpyridine was oxidized with iodobenzene diacetate–potassium hydroxide–methanol as described in ref. 8, to give the acetal (**14**) (45—50%); m.p. 88—89 °C. 6M-HCl (40 ml) was added to the acetal (**14**) (1.83 g) in water (20 ml) and the resulting solution was left at room temperature for 20 h. The solution was neutralized with an excess of solid sodium hydrogen carbonate, saturated with ammonium chloride, and extracted with dichloromethane (5 × 75 ml). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure and the crude product was recrystallized from acetone (0.96 g, 70%), m.p. 112—113 °C. The spectral data on product (**9**) prepared according to the general procedure (oxidation of silyl enol ether) and from the hydrolysis of acetal (Scheme 1) were essentially identical.

2-*Hydroxyacetylfuran* (**10**).—A colourless crystalline solid m.p. 82—83 °C (lit., m.p. 81—82 °C, Table 1, ref. *k*) was obtained by addition of hexane to the oily crude product; δ($CDCl_3$) 3.40 (1 H, t, OH; disappears with D_2O), 4.78 (2 H, d, CH_2OH; collapses to singlet with D_2O), 6.63 (1 H, m, furan), 7.35 (1 H, d, furan), and 7.79 (1 H, br, furan).

2-*Hydroxyacetylthiophene* (**11**).—The silyl enol ether (**6**) (2.10 g, 10 mmol) was added to a stirred and cooled (0 °C) mixture of iodosobenzene (2.42 g, 11 mmol) and boron trifluoride–diethyl ether (2.84 g, 20 mmol) in water (125 ml) and the mixture stirred for 2 days at room temperature. Work-up of the reaction mixture followed by addition of hexane caused separation of a solid which contained *ca.* 20% of the coupling product 1,4-di(2′-thienyl)butane-1,4-dione (indicated by the presence of a characteristic peak at δ 3.4 in the ^1H-n.m.r.). Recrystallization with hexane (2 ×) yielded pure crystalline product (**11**) (0.71 g, 50%), m.p. 73—74 °C (lit., m.p. 73—74 °C, Table 1, ref. *l*); δ($CDCl_3$) 3.46 (1 H, t, OH; disappears with D_2O), 4.82 (2 H, d, CH_2OH; collapses to singlet with D_2O), 7.23 (1 H, m, thiophene), and 7.80 (2 H, m, thiophene).

2-*Hydroxyacetylbenzofuran* (**12**).—This compound was prepared according to the general method. Addition of hexane to the crude oily mixture caused separation of a solid which showed a small amount (10%) of the coupling product. Pure crystalline product (**12**), m.p. 127—128 °C (lit., m.p. 128—129 °C, Table 1, ref. *m*) was obtained by recrystallization from ethanol (2 ×); δ($CDCl_3$) 3.30 (1 H, t, OH; disappears with D_2O), 4.90 (2 H, d, CH_2OH; collapses to a singlet), and 7.65 (5 H, m, benzofuran).

2-*Acetoxyacetylpyridine* (**15**).—A solution of 2-hydroxyacetylpyridine (**8**) (1.37 g, 10 mmol) prepared from the oxidation of 2-acetylpyridine silyl enol ether (**3**) and acetic anhydride (1.5 ml) in dry acetonitrile (25 ml) was refluxed for 5 h. The solvent was evaporated under reduced pressure and the resulting residue poured into crushed ice (*ca.* 50 g).

* The ketones (**8**) and (**9**) were converted into corresponding oxime methiodides. The properties of these oxime methiodides along with the results on acetylcholinesterase re-activation studies will be published elsewhere.

Neutralization with sodium hydrogencarbonate followed by extraction with dichloromethane yielded (**15**) (1.52 g, 85%) as an oil which was crystallized from hexane; it had m.p. 43—44 °C (lit.,[8] m.p. 43—43.7 °C). δ($CDCl_3$) 2.08 (3 H, s, –OCO*Me*), 5.48 (3 H, s, CH_2OAc), 7.35 (1 H, m, pyridine), 7.75 (2 H, m, pyridine), and 8.65 (1 H, d, pyridine).

3-*Acetoxyacetylpyridine* (**16**).—This compound was prepared by acetylation of compound (**9**) according to the conditions described for compound (**15**). It had m.p. 84—85 °C (EtOH) (lit.,[9] m.p. 84—85 °C); δ($CDCl_3$) 2.07 (3 H, s, OCO*Me*), 5.28 (3 H, s, CH_2OAc), and 7.34—9.08 (4 H, m, pyridine).

Acknowledgements

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